THE UNIVERSITY OF ALBERTA

" THE PYROLYSIS OF PROPANE IN A SURFACE COMBUSTION

AUTOTHERMIC REACTOR"

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The undersigned hereby certify that they
have read and recommend to the Faculty of Graduate
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A B S T R A C T

     A surface combustion autothermic reaction furnace was designed and built in order to determine its suitability for the thermal decomposition of light hydrocarbons. The unit was used to produce ethylene by thermally decomposing propane. Propane was used to test the unit because it cracked at temperatures easily obtained in the furnace, and because of the ease with which it could be handled.

     The product distribution obtained from thermal decomposition of propane in this unit corresponded approximately with the product distributions obtained in other processes. Thermal efficiencies were relatively low. However, the major heat losses present in this unit were of the type that could be reduced considerably when "scaled up" to commercial size units. The future of this process depends on economic factors beyond the scope of this thesis.

ACKNOWLEDGEMENT

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INTRODUCTION

Various investigators in the past have been interested in the production of ethylene. This is due to the industrial importance of ethylene as a chemical building block. At present, the production of ethylene by the tubular furnace is the dominant process, but other methods have been proposed which may yield even cheaper ethylene. One such method is by means of autothermic pyrolysis. This is simply a process wherein the heat required for decomposition is generated in situ. The process is consequently self-sufficient.

During World War II Germany used autothermic techniques for the production of ethylene from ethane and oxygen. The process was carried out at approximately 0.5 atmospheres absolute pressure. After the World War R. M. Deansely and C. H. Watkins (3) in the United States studied the process on a pilot plant scale. They found that there was no real need for subatmospheric operation with its attendant increased costs. Furthermore, with proper attention given to heat exchange and thermal economy, air may be used rather than oxygen. Although at the time (1951) the process appeared to be competitive with conventional methods, no industrial plants have yet been built in America.

Recent experience in the Research Council of Alberta laboratories indicated that a surface combustion burner would be

an efficient way of supplying the heat necessary for thermal decomposition of hydrocarbons.

The process is carried out by simply mixing the hot combustion product gases from the burner with the hydrocarbon feed as illustrated in Figure 1. Separation of combustion reactions from cracking reactions appears to offer several advantages over conventional autothermic techniques. First, a cheap fuel may be burned rather than part of the feed. Second, combustion is essentially complete at the burner surface, and the "reforming" reactions between the carbon dioxide and water (formed during combustion) and the hydrocarbon feed are slow compared to the cracking reactions. There is, therefore, a good chance that the carbon monoxide - to - carbon dioxide ratio would be lower, resulting in higher thermal efficiencies. There have been several patents in which a premixed blow torch type of burner is introduced directly into the reaction zone. Flame temperatures in such a case are very high causing excessive carbon formation. Further, it is difficult to stabilize a flame in the gas phase. On the other hand, the surface combustion burner is capable of producing stable and complete combustion at relatively low temperatures.

The work reported here included the design of a surface combustion reactor and its application to the thermal decomposition of propane.

THEORETICAL CONSIDERATIONS

1. Surface Combustion

Sir Humphrey Davy first observed low temperature catalysis
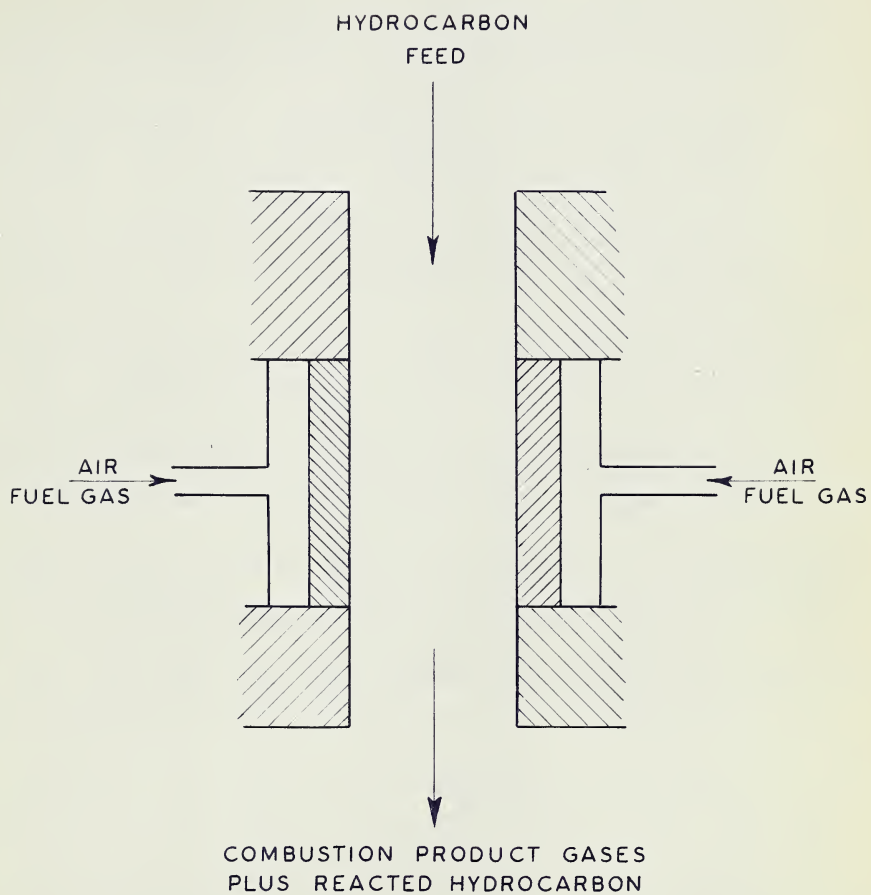
FIG. I SCHEMATIC REACTION FURNACE

in 1817 when he inserted a piece of warm platinum wire into
a non-explosive mixture of oxygen and coal gas. He found that the
platinum wire glowed and became hot. Other investigators, later
on, discovered that various other metals and metallic oxides ex-
hibited the same property as platinum with regards to low temper-
ature catalysis. It was, however, Luke (10) who really started
a systematic investigation of surface or flameless combustion.
Luke worked on the idea that an explosive mixture of oxygen and
gas when ignited would form a stable flame front on a solid surface.
He noted that a screen or porous plate would prevent to some extent
the flame front from travelling past it, provided the heat evolved
in the very rapid reaction could be dissipated. Failure to dissi-
pate this heat leads to what is called "back-flashing" or "back-firing".
It was known then that flame movement was markedly damped by movement
through small openings. Thus Luke designed and patented two types
of surface combustion burners. Figure 2 (a) is an example of an
explosive mixture of air and fuel gas impinging and burning on a
bed of refractory chips. Figure 2(b) is an example of the explosive
mixture of air and fuel gas passing up through a bed of refractory
chips in which the burning takes place.

Bone (1,9) in England worked on the same problem and part
of the work was done on a porous refractory diaphragm. Here, it was
noticed that when the explosive mixture is first lit, there is a
small flame in front of the plate (porous diaphragm). This flame re-
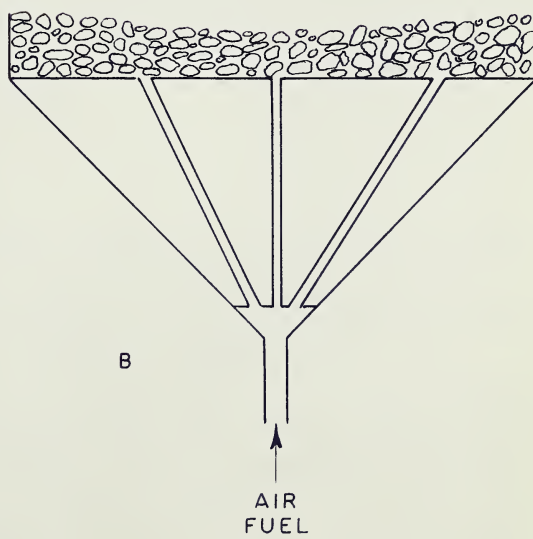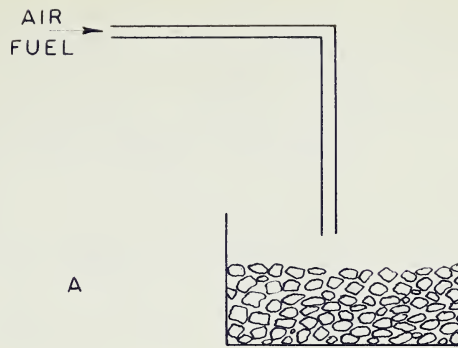
FIG.2   LUKE'S   SURFACE   COMBUSTION   BURNERS

ceded to the surface after the plate became hot giving surface com-
bustion. This is the fore runner of the surface combustion burner
used in the present investigation. Excessive surface temperatures
caused "back-flashing", often damaging the plate.

Further discussion of surface combustion requires some
knowledge of the theory of flames (8), particularly that of flat
flames. The surface combustion burner used resembles, in many ways,
a flat flame burner.

A flame is essentially a fast, high temperature oxidation
that is generally regarded as a free radical reaction. This oxidation
is controlled by external factors, such as burner design, initial gas
temperature, and turbulence of the combustible mixture, as well as by
the composition and other characteristics of the fuel. A flame may
be considered to consist of three zones:

1. Burned gases

2. Luminous

3. Preheat

Figure 3 shows a Bunsen burner flame in which the zones are not closely
delineated. The flat flame studied to give the temperature distribution
illustrated in Figure 4 was of a special type.

To experimentally study flat flames, special techniques and
burners have been employed. Figure 4 illustrates the temperature dis-
tribution in a typical flat flame. In this particular case, the propane-
air flame was a very lean, wide, essentially flat, motionless, low-
temperature flame. Conditions were deliberately chosen to give a thick

1. BURNED GASE ZONE
2. LUMINOUS ZONE
3. PREHEAT ZONE

FIG. 3   BUNSEN BURNER FLAME

FIG. 4

TEMPERATURE DISTRIBUTION THROUGH
A FLAT BURNER FLAME
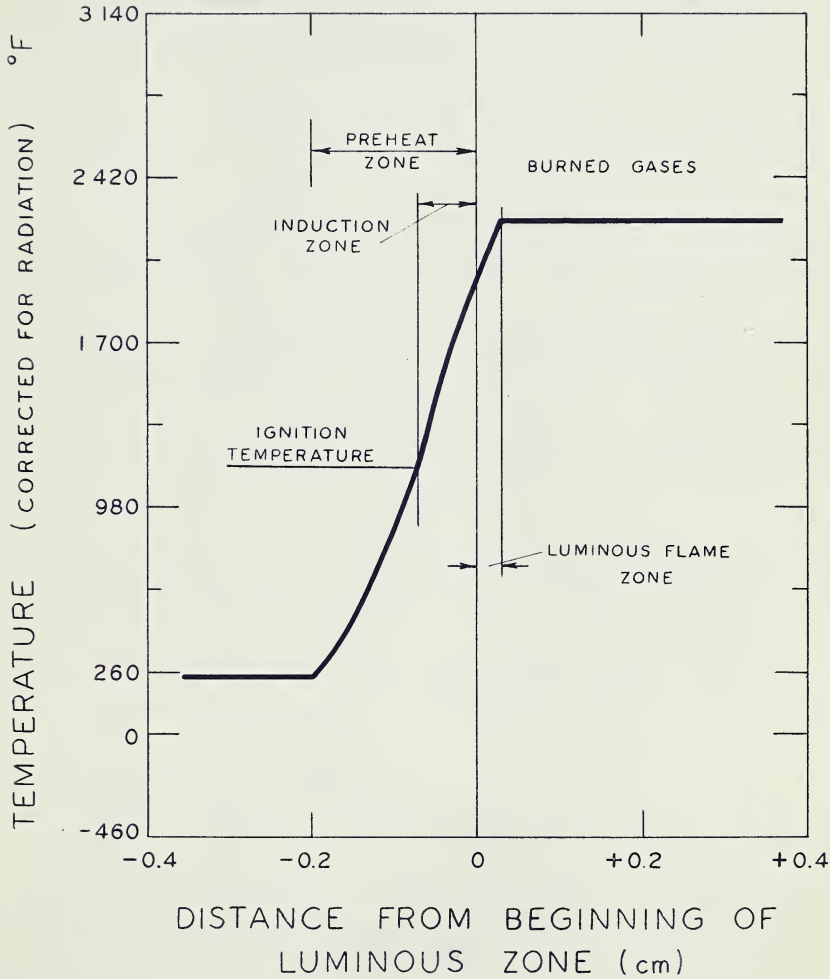
enough flame that a temperature traverse could be made. Normally
flames are not this thick. The burned gas zone contains the products
of combustion produced in the luminous zone. There are no temperature
or concentration gradients in this zone. The luminous zone is the region
between the burned and unburned gases. The thickness of this boundary
may vary widely - the more rapid the combustion the thinner the flame
front or boundary. The rate at which the flame front moves back towards
the unburned gases is called the flame velocity and is one of the import-
ant parameters in the combustion process. The position of the flame
front in space is determined by the vectorial sum of the flame velocity
and the flowing velocity of the unburned gases. The flame front will be
stabilized when the two velocities are equal - a condition that exists,
for example, at the exit of a Bunsen burner.

  The tendency of a flame to flash back through the unburned
mixture may be explained by either of two flame combustion theories
- one based on purely thermal grounds, and the other on chemical re-
action grounds. The so-called comprehensive theories of combustion
take into account both mechanisms.

  In the simplified thermal theory the combustible gases in
the preheat zone are heated by conduction from the flame front. When
these gases reach ignition temperatures, which may be as low as 1200° F,
they burn and the flame front moves back. The onset of combustion is
due to a rise in temperature of the unburned gases.

  In the chemical activation theory, the onset of combustion
in the preheat zone is due to a backward diffusion of free radicals

which are in relatively high concentrations in the flame zone. (7)
There is a concentration gradient of free radicals very similar to
the temperature gradient shown in Figure 4.

Both theories accept the role of free radicals as being
responsible for the combustion process. Their presence in the preheat
zone may be caused either by thermal means or by diffusion. It is
generally agreed that there is a definite induction period before
the combustible gas burns. This induction period explains why the
unburned gases, upon reaching ignition temperatures in the preheat
zone, do not burn until they reach the flame zone. Higher gas velo-
cities enable the unburned gases to pass through the preheat zone in
a shorter time due to two additive effects - a shorter preheat zone
and a faster velocity through it. If the time interval between the
point at which the unburned gases reach ignition temperature and the
point at which it enters the flame zone is shorter than the induction
period, then the flame will not flash back.

In surface combustion the general theory regarding the flames
apply. Here, the unburned gases pass through a permeable ceramic
burner plate and the flame front is stabilized at the burner surface.
Due to the catalytic effect of this surface, it is possible to get
stable combustion at relatively low temperatures. A temperature
gradient exists in the interior of the plate similar to that shown in
Figure 4. However, since the thermal conductivity of the burner
material is orders of magnitude higher than that for gas, the preheat
zone is stretched out, and so is the ignition zone. Although the

actual width of the preheat and ignition zones in a surface combustion burner are larger than in a gas flame, the actual velocity of combustible gases is higher, for the same mass flow, since the cross-sectional area for flow is reduced due to the burner plate. With the burner used in the present investigation, in order to keep the residence time of the combustible gases in this ignition zone smaller than the induction period the surface combustion flame temperature had to be kept at significantly lower values than that encountered in open flames.

The temperature at the surface of the burner plate is determined by:

1. the rate of fuel and air flow, which determines the heat input to the system, and

2. the rate at which the surface is able to dissipate the heat to the surroundings.

A heat balance on the surface given the equilibrium temperature. The relationship between surface temperature and fuel rate is shown graphically in Figure 5. Air and natural gas, in stoichiometric quantities enter the burner at room temperature (77° F). Heat dissipated is assumed to be entirely due to radiation to surroundings at room temperature. Thus, at a combustible gas flow rate of 4 SCFM/sq. ft., the surface temperature is at 1370° F; at 8 SCFM/sq. ft., the surface temperature becomes 1660° F. However, if the burner is completely enclosed and the combustion made adiabatic, then the temperature at the surface of the burner will approach the theoretical flame temperature of 3500° F.

FIG. 5

SURFACE TEMPERATURE OF BURNER
VS. TOTAL FLOW RATE
(BURNER RADIATING TO SURROUNDINGS AT 77°F)

AIR + CH$_4$ AT 77°F

TEMPERATURE °F

TOTAL FLOW (SCFM PER FT.^{2} BURNER SURFACE)
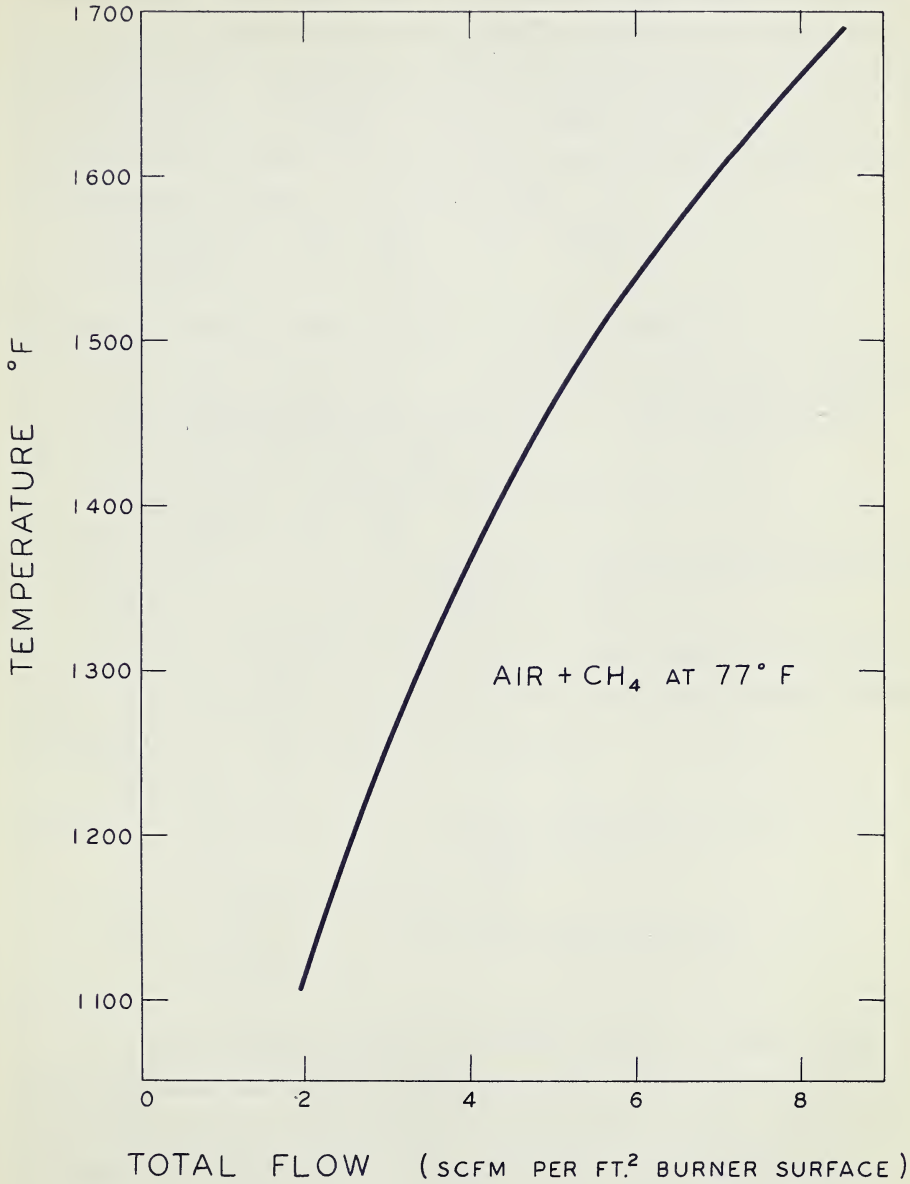
For steady state operation, and assuming that the gaseous mixture of air and gas is at thermal equilibrium with the burner plate at all times and that the mass heat capacity (GCp) is independent of temperature, the theoretical temperature distribution through the burner plate may be calculated. The detailed derivation of the equation for the theoretical temperature distribution is shown in the Appendix. It is obtained by writing a heat balance for an incremental section of burner plate of unit cross-sectional area in the preheat zone. The differential equation is of the form:

$$ k \frac{d^2 T}{dx^2} + GCp \frac{dT}{dx} = (r)\ (\triangle H) $$

where k = thermal conductivity of burner material

G = mass rate of flow of combustible gases, lb. moles/(hr)(sq.ft.)

C_p = average molal heat capacity of combustible gases, BTU's/(lb. mole)^{o}F.

x = distance from surface of burner, ft.

T = temperature, ^{o}F.

r = f(T) = rate of reaction, lb. moles converted/(hr)(cu.ft)

$\triangle H$= heat of reaction, BTU's/lb. mole

The simplest assumption is that there is no reaction in the preheat zone, in which case the right hand side of the equation becomes zero. Integration of the equation then gives:

$$ (T_s - T) = (T_s - T_a)\ (1 - e^{-\alpha x}) $$

where T_a = temperature of entering combustible gases, ^{o}F (in this case, say 77°F or room temperature)

T_s = surface temperature ^{o}F

α = $\frac{G C_p}{k}$, a dimensionless parameter

The shape of the temperature profile in the preheat zone is a function of the surface temperature T_s as well as the parameter α. The curves of the temperature profiles for various values of α are shown in Figure 6. The larger values of α give high temperature gradients near the surface, which help to prevent flash-back by shortening the time interval during which the combustible gases are at ignition temperatures. High mass rates of flow and low burner plate thermal con –

FIG. 6

THEORETICAL TEMPERATURE DISTRIBUTION
THROUGH BURNER PLATE

(FOR SURFACE TEMPERATURE OF 2 000° F)
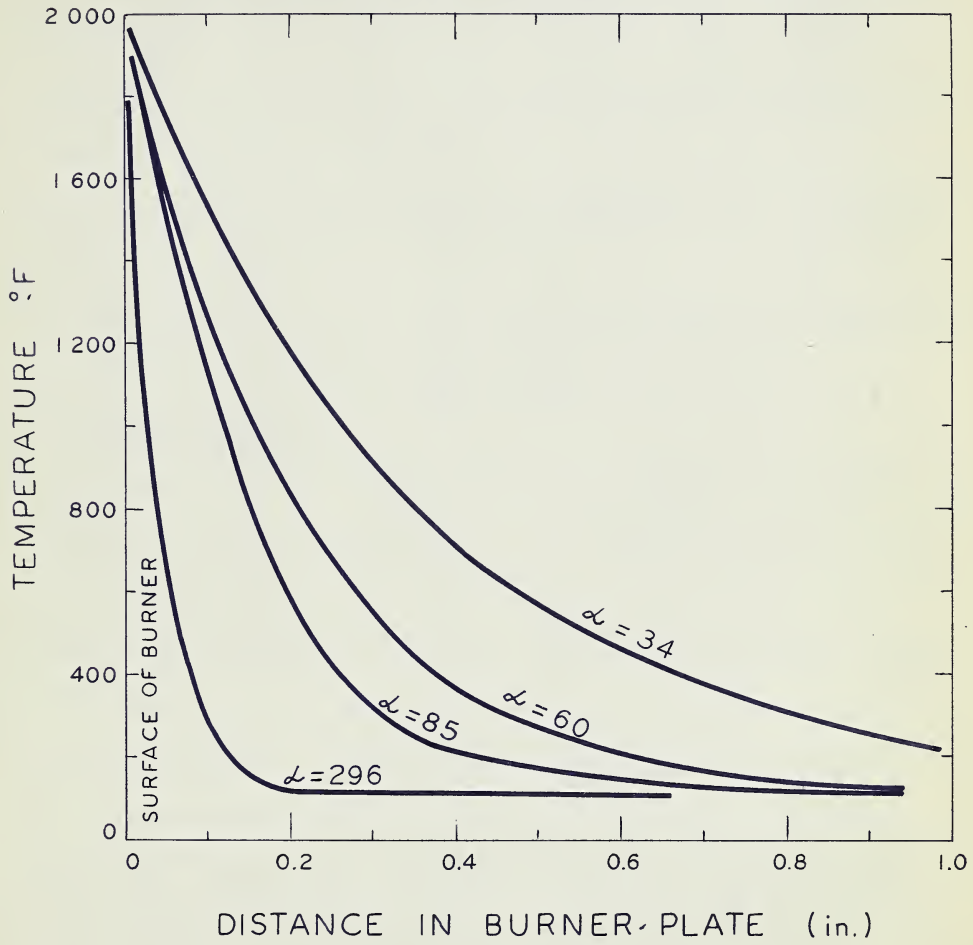
ductivity are therefore desirable. The values, $\alpha = 34$ and $\alpha = 65$, represent approximately the values of the parameters for two of the flow rates actually used experimentally in the present investigation.

Flash-back is the result of the inability of the system to dissipate the heat produced. The heat that is not dissipated increases the temperature of the surface of the burner. With an increase in this temperature there is a general temperature increase throughout the plate, eventually causing pre-ignition of the combustible gases before they reach the surface. The heating effect progresses cumulatively once it has started. Flash-back, when it does occur, does so in a matter of seconds. The flame front travels from the burner front to the back very quickly and ignites the combustible mixture entering the burner.

2. Propane Pyrolysis

The unit was built in an attempt to evaluate the possibility of using this type of heat source for the thermal decomposition of light hydrocarbons. While a wide variety of hydrocarbons may be pyrolyzed it is generally known that the lower the molecular weight of the feed stock, at least down to ethane, the higher the yield of ethylene possible. However, these lower hydrocarbons require more severe conditions of time and temperature, particularly the latter (3). Commercially, propane and ethane are the two favored hydrocarbons for making ethylene by pyrolysis. Propane was used here because it could be pyrolyzed at temperatures easily attained in the furnace. It is also easier to store and handle then ethane, which requires very high pressures to maintain it in the liquid form at room temperatures.

(a) <u>Kinetics</u>

In the thermal decomposition of propane there are a great many possibilities for the occurrence of various reactions. These reactions may be affected by temperature, pressure, and contact time. Table 1 (11) lists effective overall reactions encountered in propane pyrolysis.

The relative rates of these reactions determines the product distribution. For example, at 1350° F and 1 atmosphere pressure the rates of reactions 1, 2, 3 and 4 (the primary reactions) are in the ratios 1.0: 0.26: 0.87: 0.04. Reactions 1 and 3 are, therefore, the major ones. Myers and Watson (11) solved a typical reactor design problem by two methods: - first, by using all ten equations and, second, by using only the first four reactions. They found no significant difference in their answers and concluded that in predicting product distribution, the last six reactions may be neglected.

At low conversions, all the primary reactions are assumed to be first order; hence the product distribution should not be pressure sensitive. It has been found experimentally that there is no noticeable change in product distribution when the pressure is varied from one to seven atmospheres.

Since the reactions have different activation energies, then temperature would have a significant effect upon product distribution. Of four primary reactions, reactions 1 and 2 become more important relative to reactions 3 and especially 4 as the temp-

TABLE 1

Effective Overall Reactions in Propane Pyrolysis

1. $C_3H_8 \longrightarrow C_2H_4 + CH_4$

$$r = k \, \pi \, \frac{n \, C_3 \, H_8}{n_t} \; ; \quad \text{(moles propane)}$$

$A = 3.0158 \times 10^{14}$ $\qquad \Delta H^* = 66,500$

2. $2 \, C_3H_8 \longrightarrow C_2H_6 + C_3H_6 + CH_4$
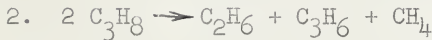
$$r = k\pi \, \frac{nC_3 \, H_8}{n_t} \; ; \quad \text{(moles of propane)}$$

$A = 3.6745 \times 10^{13}$ $\qquad \Delta H^* = 65,000$

3. $C_3H_8 \rightleftharpoons C_3H_6 + H_2$
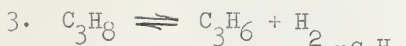
$$r = k \, \pi \left[\frac{nC_3H_8}{n_t} - \frac{nC_3H_8 \, n \, H_2 \; \pi}{n_t^2 \; K} \right] ; \quad \text{(Moles of propane)}$$

$A = 9.989 \times 10^{12}$ $\qquad \Delta H^* = 60,000$

$\Delta H^o_{1300} = 30,505$ $\qquad \Delta S^o_{1300} = 32,85$

4. $2C_3H_8 \rightleftharpoons C_2H_6 + C_4H_{10}$
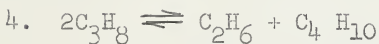
$$r = k \, \pi \left[\frac{n \, C_3 \, H_8}{n_t} - \frac{n \, C_2H_6 \, n \, C_4H_{10}}{n_t^2 \; K} \right] ; \quad \text{(Moles of Propane)}$$

$A = 2.490 \times 10^{10}$ $\qquad \Delta H^* = 54,000$

$K = 1.30$ (substantially independent of temperature)

5. $C_3H_6 + H_2 \longrightarrow CH_4 + C_2H_4$

$$r = k\pi \, \frac{nC_3 \, H_6}{n_t} \; ; \quad \text{(moles of propylene)}$$

$A = 5.266 \times 10$ $\qquad \Delta H^* = 38,000$

6. $C_3H_6 \longrightarrow 0.149 \, CH_4 + 0.064 \, C_2H_2 + 0.2555 \, C_2H_4$

$\qquad + 0.085 \, C_5H_8 + 0.2555 \, C_4 \, H_8$

$\qquad + 0.0745 \, C_6H_{10} + 0.0745 \, H_2 + 0.053 \, C_2H_6$

$\qquad + 0.053 \, C_4H_6$
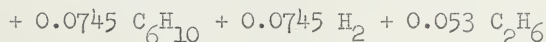
TABLE 1 (cont.d)

$$\dot{r} = k \pi \frac{nC_3 H_6}{n_t} \quad ; \text{(moles of propylene)}$$

$$A = 2.746 \times 10^{12} \qquad \Delta H^* = 56,000$$

7. $C_4 H_{10} \longrightarrow 0.12 H_2 + 0.49 CH_4 + 0.39 C_2 H_4 + 0.38 C_2 H_6$

$$+ 0.49 C_3 H_6 + 0.01 C_3 H_8 + 0.12 C_4 H_8$$
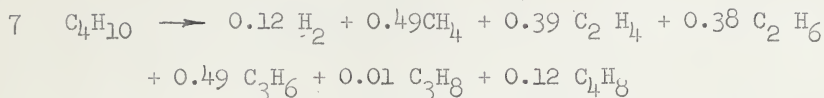
$$r = k \pi \frac{nC_4 H_{10}}{n_t} \quad ; \text{(moles of butane)}$$

$$A = 4.78 \times 10^{14} \qquad \Delta H^* = 63,000$$

8. $C_2 H_6 \rightleftharpoons C_2 H_4 + H_2$

$$r = k \pi \left[\frac{n C_2 H_6}{n_t} - \frac{n C_2 H_4}{n_t^2} \frac{n H_2 \pi}{K} \right]$$

$$A = 9.83 \times 10^{12} \qquad \Delta H^* = 63,000$$

$$\Delta H^o_{1300} = 34,316 \qquad \Delta S^o_{1300} = 32.12$$

9. $C_4 H_8 + H_2 \longrightarrow CH_4 + C_3 H_6$
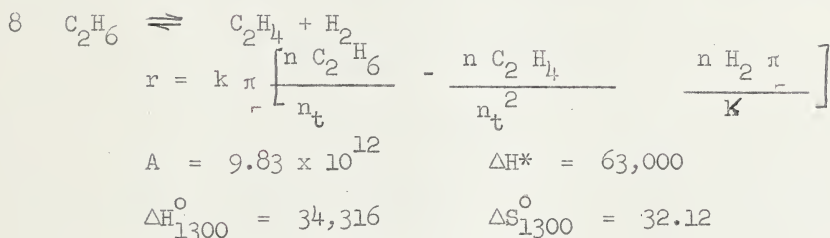
$$r = k \pi \frac{n C_4 H_8}{n_t} \quad ; \text{(moles of butane)}$$

$$A = 4.743 \times 10^{15} \qquad \Delta H^* = 67,000$$

10. $0.287 C_2 H_2 + 0.333 C_6 H_{10} + 0.38 C_5 H_8 \longrightarrow 0.472 C_6 H_6$

$$+ 0.91 CH_4 + 0.333 C_2 H_4 + 0.178 C$$
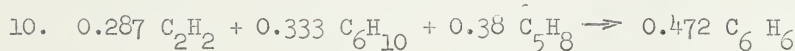
$$r = k \pi^2 \left[\frac{NH \ HC}{n} \right]^2 ; \text{(moles of total reactant)}$$

$$A = 9.34 \times 10^9 \qquad \Delta H^* = 35,000$$

where

$$\pi = \text{total pressure (atm.)}$$

$$k = A e^{\Delta H^*/RT}$$

TABLE 1 (continued)

π = total pressure   (atm.)

$k = Ae^{\Delta H^*/RT}$

k = Reaction velocity constant   (lb moles)/(cu.ft.)(hr.)(atm.

ΔH^* = Apparent enthalpy of activation   BTU/(lb.mole)

R = Gas constant   BTU/(lb.mole)($^{\circ}$R)

E = Apparent energy of activation   BTU/(lb.mole)

A = Apparent frequency factor

$K = e^{(-\Delta H^{\circ}1300/RT) + (\Delta S^{\circ}1300/R)}$

K = Equilibrium constant

ΔH° = Standard enthalpy   BTU/(lb.mole)

ΔS° = Standard entropy   BTU/(lb.mole)($^{\circ}$R)

r = Rate of reaction   (lb.moles)/(cu.ft.)(hr.)

erature is increased. The net effect is that at higher temperatures, ethylene is favored over propylene. However, in most industrial processes, the conversion does not take place isothermally (in the conventional tube furnace, for example, the temperature increases with the fractional conversion so as to maintain a relatively constant overall reaction rate); and the effect of temperature is masked. It is more common in such cases to try and correlate product distribution as a function of fractional conversion. .

(b) Industrial Processes

The Tubular Furnace (12)

The tubular furnace is designed so that the feed stock to be thermally cracked is heated, as it passes through the pyrolysis tubes in the furnace. The tubes are 3 to 5 inches inside diameter and made of stainless steel. The reason for this range in tube diameters is to get reasonable surface to volume ratios. The tubular requirements for a furnace are based on a heat transfer rate of approximately 125 to 200 BTU/(hr.) (sq. ft.)($^\circ$F). Average radiant heat intensities from 9000 to 11000 BTU/(hr.) (sq. ft.) are employed in operating pyrolytic furnaces having tubes located near the refractory wall.

Advantages

The operation is straight forward.

Disadvantages

The materials of construction are expensive and have to be periodically replaced. The formation of carbon on the tube walls

causes operational difficulties.

The Pebble Bed (Thermofor) Furnace (4)

      This is a continuous regenerating process wherein the pebbles flow countercurrent to the reacting hydrocarbon. The operation consists primarily of two units. In one, the heater, the cool pebbles are brought in by a bucket conveyor and heated by an air-fuel gas flame. Any carbon that may have deposited on the pebbles is burned off. The hot pebbles fall into the second or reaction unit. In this unit the reacting hydrocarbon enters at the bottom and is heated by the pebble bed as it goes through. The cold pebbles at the bottom of the reaction unit drop down on to a bucket conveyor. This process depends upon the sensible heat of the solid.

Advantages

      High thermal efficiencies; comparatively cheap material of construction.

Disadvantages

      A variable temperature range exists within the reaction unit.

      The difficulties of handling and control of hot solids.

Wulff Process (6(a))

      This process is made up of two identical units built of refractory material so that there is a maximum surface to volume ratio. The checker work of refractory material is heated in a cyclic operation with an air-fuel gas flame. Thus, one side of

the furnace is being heated while the other side is decomposing the
reacting hydrocarbon. When the temperature of the reaction side drops
sufficiently the hydrocarbon is sent into the hot side while the
cooled side is heated up. This process also depends on the sensible
heat of the solid to supply the endothermic heat of cracking.

Advantage

High thermal efficiencies.

Disadvantages

Cyclic operation. The reaction occurs over a range of temp-
eratures.

Lead Bath Process (6)

The molten lead bath process utilizes the heat transferred
from the molten lead to the hydrocarbon that is bubbled through it to
decompose the hydrocarbon. With the heaters outside the reaction
furnace it is necessary to rely on the heat transfer from the outside
through the reaction vessel and molten lead to the reacting hydro-
carbon. The inside heat transfer coefficients (based on calculated
heat flux, corrected inside wall temperatures and lead temperatures)
were of the order of 150 to 250 BTU/(hr.) (ft^2) $(^oF.)$ Thus the low heated
surface to volume ratio for the reactor appeared to be favorable.
There was little coke formation.

Advantage

There is very good heat transfer between the lead and the
gas and, therefore, the reaction vessel is compact.

Disadvantages

The flow rate of the reacting gas is limited due to possible entrainment of molten lead in the exit stream.

The temperatures used are limited by the vapor pressure of the lead.

The use of molten lead.

Conventional Autothermic Process (3)

The autothermic process is one wherein the hydrocarbon to be decomposed is burned in a deficient amount of oxygen or air. Part of the hydrocarbon is utilized to produce the heat necessary for thermal decomposition of the unburned portion. The CO to CO_2 ratio in the product gas from this process is approximately 2 with the range being from 1.85 to 2.54. The use of oxygen instead of air does not give a significant difference in the yields. Naturally there is a difference in concentration because, when oxygen is used there is no nitrogen for dilution. This process utilizes the effective heat transfer between combusting and decomposing gases.

Advantages

The reactor volume is small.

It is possible to attain high temperatures.

The materials of construction may be cheap.

Disadvantages

There are a great many side reactions leading to C and C_{4+}.

Dilution of the off gases if air is used or the cost of oxygen if it is used.

TABLE 2.   Comparison of Major Products in Propane Pyrolysis

Moles /100 moles C_3H_8 Reacted

Product	Autothermic Furnace	Tubular Furnace	Lead Bath Furnace	Pebble Furnace
C_2H_4	69.0	54.1	62.1	63.5
C_3H_6	18.6	18.2	20.4	13.8
CH_4	67.0	69.7	80.5	77.5

These comparisons are made at overall propane conversions of 80% with the exception of the Pebble Furnace Process for which data were available only at 93% conversion.

Description of Equipment

A schematic diagram of the experimental unit is illustrated in Figure 7. The unit may be divided into various parts, namely:

1. Fuel System

2. Reactor gas System

3. Furnace

4. Exhaust System

1. Fuel System

The controls for the fuel system are situated in one separate section. Air used to premix with the gas is brought in at about 80 psig. and passed through a water trap and Cuno micro-clean filter. The cleaned air then passes through a pressure regulator into the control section, and then into the body of the burner. A venturi type mixer mixes the air and gas.
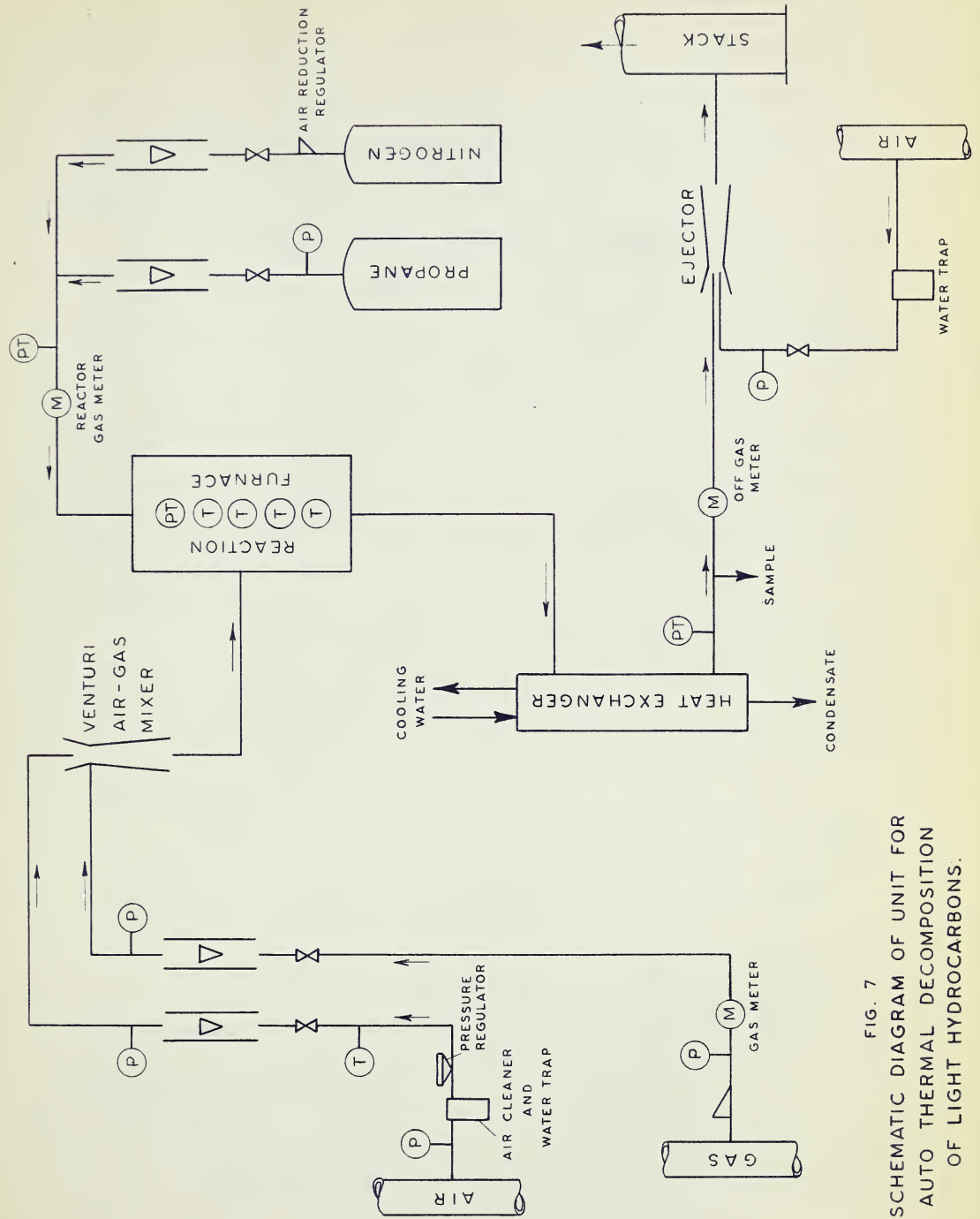
FIG. 7

SCHEMATIC DIAGRAM OF UNIT FOR
AUTO THERMAL DECOMPOSITION
OF LIGHT HYDROCARBONS.

Natural gas of varying composition but constant heating value, used in the fuel system is brought in at a pressure of about 6 psig. It is passed through a Fisher Governor regulator that reduces the gas pressure to 11.25 oz. per sq. in. gauge, before being mixed with the combustion air.

A rotameter in the line after the Fisher Governor is used to indicate the rate of flow of gas. There is an on-off solenoid valve in the line ahead of the pressure regulator that is connected to a temperature indicator with a preset controller feature. A thermocouple set against the back of the burner plate indicates this temperature. When the temperature gets too high due to a "flash-back" the solenoid valve is shut off automatically to protect the burner.

2. Reactor Gas System

In this system provision is made for the introduction of nitrogen from high pressure cylinders to clean out any combustible gas that may be present in the line. It is also possible to dilute the reactor gas with nitrogen.

Commercial propane (2.5% N_2, 9.4% C_2H_6, and 88.1% C_3H_8) is brought in as a liquid in 20 gallon cylinders. These cylinders are connected in parallel and thence to the system.

A volumetric gas meter in the line after the rotameter is used to determine the rate of flow of either nitrogen, reactor gas (propane), or a mixture of both.

3. Furnace

The furnace shell is constructed of 1/4 inch steel plate

The top of the furnace is constructed as shown in Figure 8. The
shell of the body of the furnace is constructed as shown in Fig-
ure 9. Within this shell two types of insulating bricks whose
dimensions are 9 inches by 4-1/2 inches by 2-1/2 inches were
used. The insulating bricks had a thermal conductivity of 0.31
BTU/hr. sq. ft. $^{\circ}$F/ft. Of the two types of insulating brick used
in the furnace type G 26 (good to 2600 $^{\circ}$F) is used as the inner
layer and type G 23 (good to 2300 $^{\circ}$F) is the outer layer. These
insulating bricks were installed so as to leave a reaction zone
whose dimensions are 11-15/16 inches by 11-15/16 inches by 1-5/8
inches in front of the burner. The reaction volume was 0.284 cu.
ft. The first two dimensions are fixed by the size of the burner.
The third dimension was chosen to give a retention time of the right
order of magnitude. The reaction zone is closer to the top than to
the bottom. This enables the furnace to have a "soaking" region
just below the reaction zone and above the bottom of the furnace.
This soaking zone allows for further reaction. Four chromel-alumel
thermocouples which were connected to a Brown Multipoint Recorder
were installed in the reaction zone. An observation port on the
side of the furnace permitted visual examination of the reaction
zone during operation. This port was also used in lighting the
furnace. The hydrocarbon feed passed through a preheater that was
36 inches long. This preheater was made of 1/4 I.P.S. stainless
steel pipe and was located in the top of the reaction furnace.

FIG 8
TOP OF REACTION FURNACE
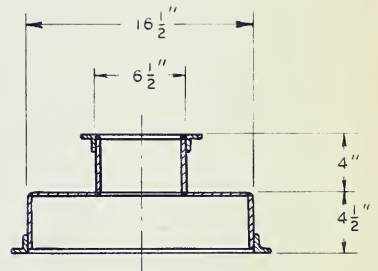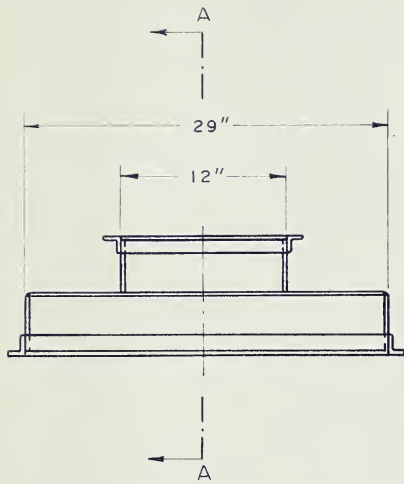
SECTION A-A
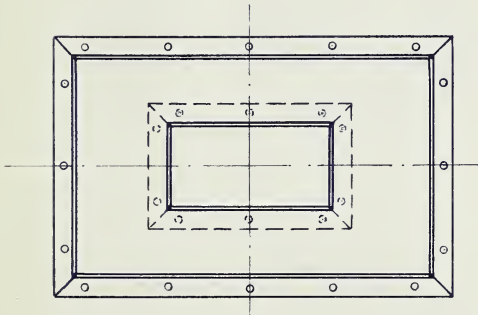
FIG. 9

BODY OF REACTION FURNACE

$\frac{1}{4}$" PIPE COUPLINGS WELDED INTO SIDE PLATE

$1\frac{1}{2}$" PIPE COUPLINGS WELDED INTO SIDE PLATE

36"

16$\frac{1}{4}$"

28"
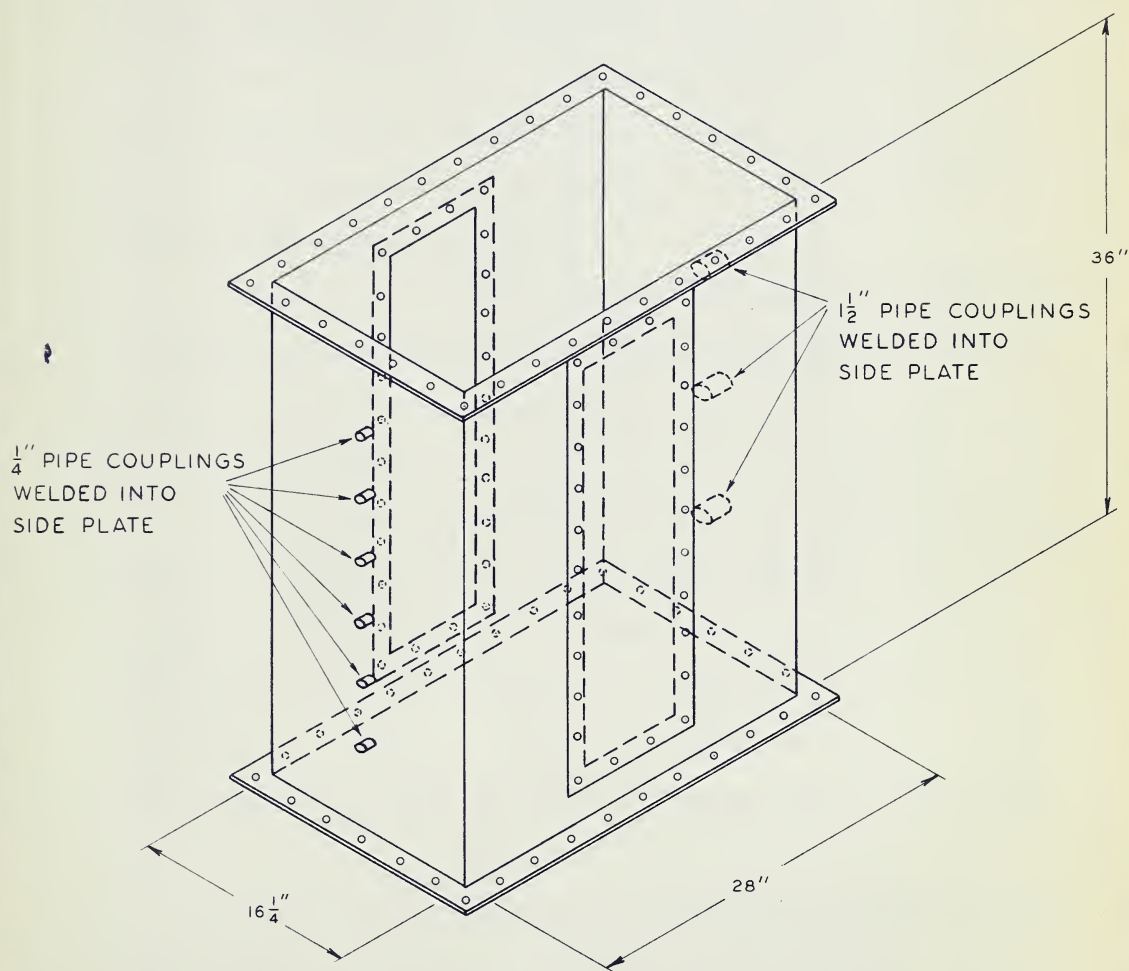
The burner (Type No. 1, rectangular) is of the Cox combustor type and manufactured by Radiant Heating of London, England. The burner plate is made of porous refractory material about 1-1/2 inches thick. This burner plate is cemented to a steel burner shell. The fuel gas entering the back of the burner shell is deflected by a distribution plate so that it is evenly distributed. Figure 10 is a cross sectional view of a burner plate. A burner of type No. 1 is specified to operate at surface temperatures of 1200° F to 1550° F releasing 50,000 BTU/(hr.)(sq.ft.).

Figure 11 is an illustration of the furnace body; Figure 12 illustrates the construction of the bottom of the furnace; Figure 13 is a photograph of the furnace.

4. The Exhaust System

The mixture of spent fuel gas and reactor gas leaves the bottom of the furnace to pass through a heat exchanger. This heat exchanger is of the shell and tube type with the gas on the shell side (six passes). The cooling water is inside the copper cooling tubes (1/2 inch tubes) (12 passes). The cooled exhaust gases then pass through a flow meter and thence through the stack to the outside air.

An air ejector draws the gases through the system and pushes them out the stack. Figure 14 is a photograph of the heat exchanger and flow meter of the exhaust system. The oxygen analyser is also illustrated here.

FIG. 10

SURFACE COMBUSTION BURNER

FIG. II
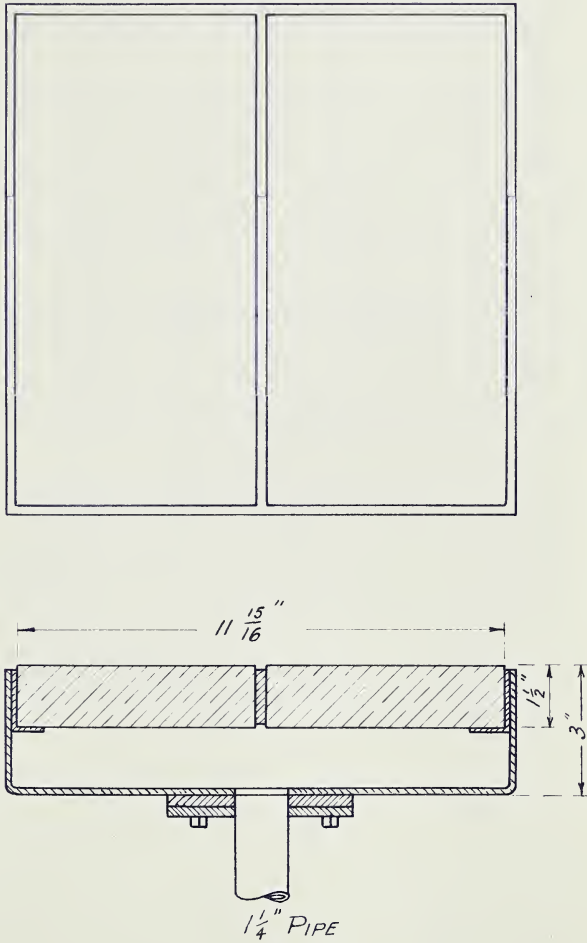
SECTIONS OF REACTION FURNACE
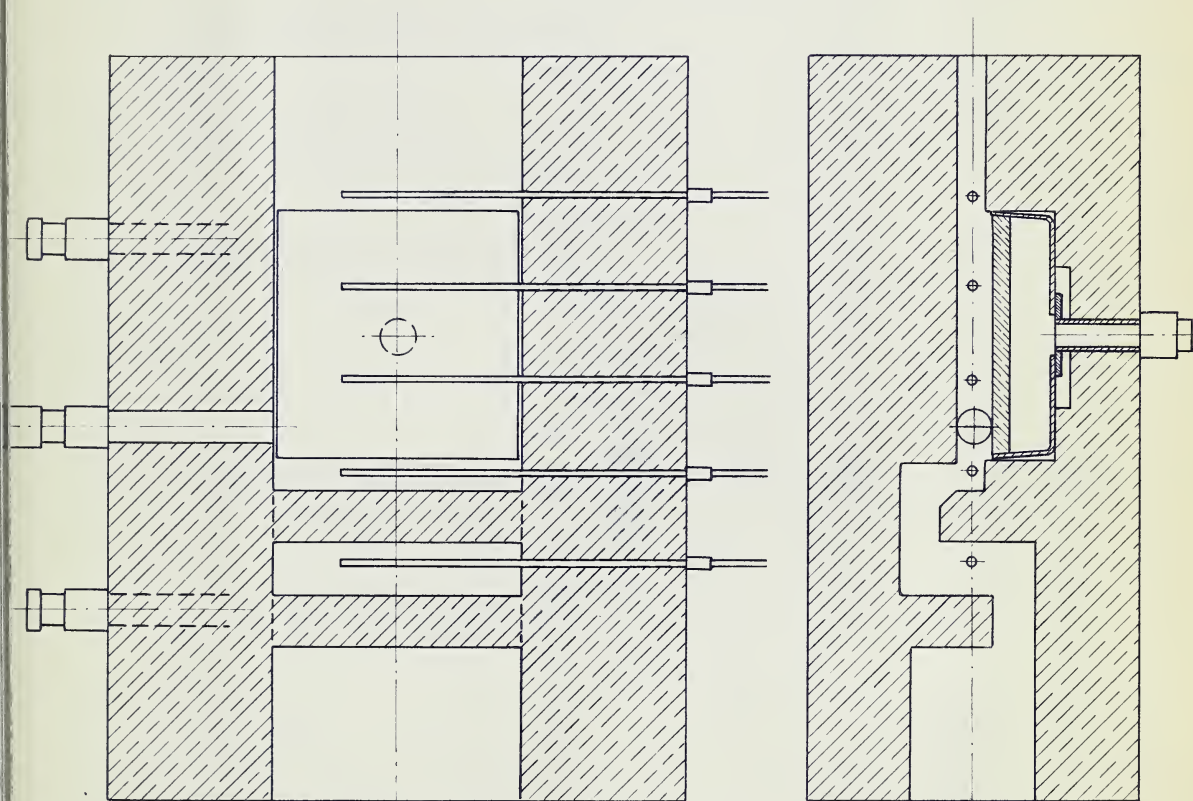
FIG. 12
BOTTOM OF REACTION FURNACE
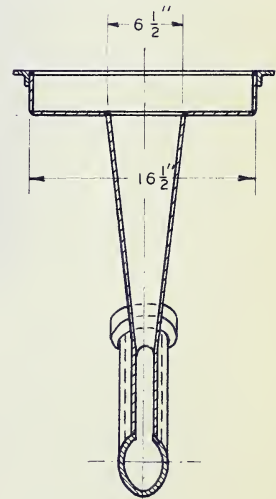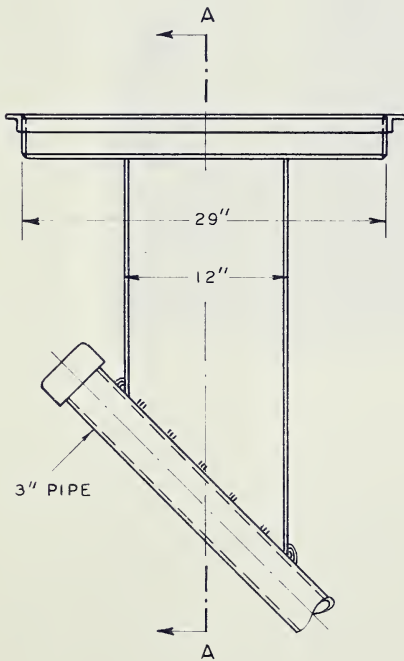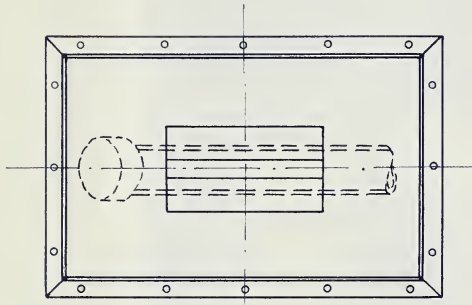
Figure 13. Photograph of Furnace
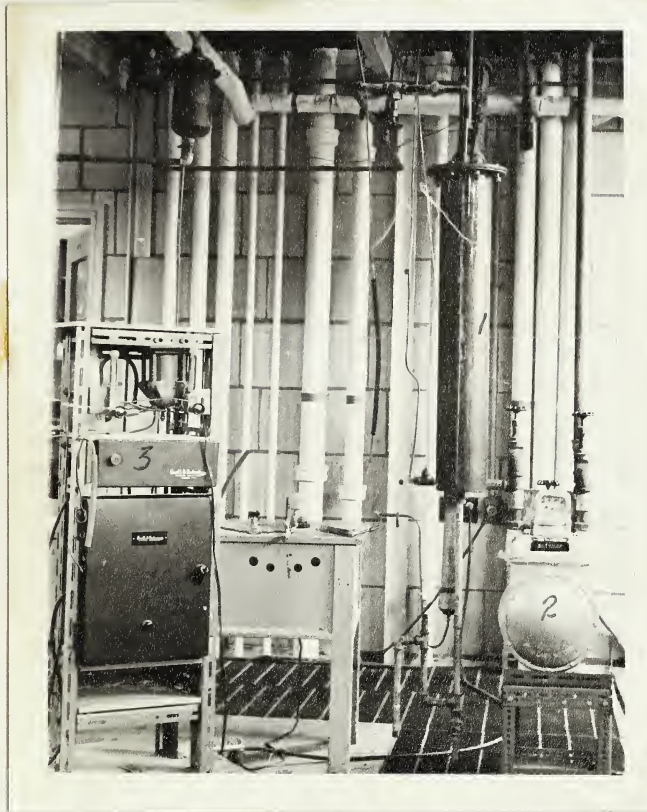
Figure 14. Photograph of Exit Gas System

1. Heat Exchanger
2. Off Gas Meter
3. Oxygen Analyser

Experimental Procedure

The air and fuel gas to the furnace were turned on. In
lighting the furnace a fuel rich mixture was used. When the burn-
ing became steady the flow of air and fuel gas were adjusted to the
stoichiometric ratio.

The pressure within the reactor proper was maintained at
approximately atmospheric pressure by adjusting controls on the gas
ejector system.

Under conditions of no heat load the furnace heated up
rapidly, and the burner surface soon reached the point where "back-
flashing" was likely to occur. Thus it was necessary to introduce
the hydrocarbon feed shortly after the burner was lit.

After the unit reached a steady state (criteria of which
included stability of reaction zone temperatures, and of the off-gas
rate), an off-gas sample was taken and all the process conditions
recorded. A typical run lasted one to two hours, after which a new
propane rate was used and another run started. The air and fuel gas
rates were held constant and a whole series of runs were made at
various propane-fuel ratios.

RESULTS AND DISCUSSION

Three series of runs were made at different fuel rates covering approximately a three-fold variation in the flow of air and natural gas. In each series runs were carried out at fuel-to-feed ratios of approximately 3, 4, 5, and 6. The data are summarized in Tables 3, 4 and 5. It must be noted that in these tables, the values reported as C_{4+} (including carbon) are calculated quantities obtained from the carbon balances by difference. They represent the carbon lost. The samples were taken in duplicate and analyzed by two methods. One method was by the Research Council of Alberta's analytical group using a Fisher-Gulf Gas chromatography unit, and the other method was by the Canadian Chemical Company's Analytical Division using a Consolidated Engineering Company Mass Spectrometer. Comparison of the two sets of analyses are given in the Appendix. The discrepancies in these analyses are significant and not readily explainable. Both methods gave good material balances, but neither showed a clear superiority. The gas chromatography analyses were chosen rather than the mass spectrometer analyses because a complete set of calculations had been made using the gas chromatography analyses before the results of the mass spectrometer analyses were available. The treatment of the data is shown in detail in the Appendix.

The introduction of propane into the reaction zone of the furnace gave no visual instability in the surface combustion on the burner. There appeared to be a wave motion of incandescent gas within the reaction zone, which moved back and forth between the burner and the inert wall opposite it.

"Flash-backs" occurred when the burner surface got too hot (1800 - 1900° F was about the upper limit). Excess temperatures were caused by high fuel-to-feed ratios as well as by the total fuel input. Thus it was possible to operate with fuel-to-feed ratios as high as 7 to 1 at the lower fuel rates while, at the higher fuel rates

TABLE 3

Surface Combustion Propane Pyrolysis Data

Series R - 11

Run No.	2	3	4	5
Fuel Gas Rate (lb. moles)/hr.	0.070	0.070	0.070	0.070
Air Rate (lb. moles)/hr.	0.67	0.67	0.67	0.67
Molal Ratio (Fuel and Air)/feed	5.95	4.93	4.04	3.04
Gas Temperatures °F				
Top of Reaction Zone	1579	1507	1407	1224
Middle of Reaction Zone	1719	1674	1609	1461
Bottom of Reaction Zone	1585	1547	1496	1385
Average of Reaction Zone	1628	1576	1504	1357
Exit of Reaction Zone	1368	1355	1323	1252
Off Gas Composition (moles)				
N_2	64.6	61.0	59.4	55.4
O_2	0.8	0.8	1.0	1.0
H_2	7.6	6.4	5.5	5.5
CH_4	8.0	9.5	8.8	7.7
C_2H_6	0.9	1.3	1.3	1.4
C_3H_8	2.4	3.6	6.1	12.0
C_2H_4	6.7	7.4	7.6	6.7
C_3H_6	0.5	1.1	1.8	2.4
CO	1.6	2.4	2.4	3.6
CO_2	6.8	6.4	6.1	4.3
Percent Expansion of Hydrocarbon Feed %	95.1	79.0	60.4	48.2
Percent Propane Reacted %	81.8	76.3	66.1	46.1

TABLE 3 (cont'd.)

Surface Combustion Propane Pyrolysis Data

Series R - 11

Oxygen Balance	%	-3.0	-0.9	+0.3	-4.5
Hydrogen Balance	%	-7.7	-5.4	-7.3	-3.6

Yields Moles/(100 moles Hydrocarbon feed)

C_2H_4	52.3	49.3	42.5	30.4
C_3H_6	4.0	7.4	9.8	10.6
CH_4	61.9	62.8	49.4	34.5

Carbon Distribution in Product %

C_2H_4	40.4	41.1	40.1	40.1
C_3H_6	4.6	9.3	13.8	21.0
CH_4	23.8	26.2	23.3	22.8
CO	2.8	3.7	3.6	3.6
C_{4+}(including Carbon)	28.4	19.7	19.2	12.5

TABLE 4

Surface Combustion Propane Pyrolysis Data

Series R - 12

Run No.		5	2	3	4
Fuel Gas Rate (lb.moles)/hr.		0.120	0.120	0.120	0.120
Air Rate (lb.moles)/hr		1.18	1.18	1.18	1.18
Molal Ratio (Fuel and Air)/feed		5.93	4.93	3.90	3.0
Gas Temperatures °F					
	Top of Reaction Zone	1441	1507	1397	1299
	Middle of Reaction Zone	1674	1627	1578	1520
	Bottom of Reaction Zone	1582	1516	1450	1418
	Average of Reaction Zone	1557	1550	1475	1412
	Exit of Reaction Zone	1366	1308	1273	1254
Off Gas Composition					
	N_2	62.3	62.9	61.4	58.3
	O_2	1.4	1.0	1.3	0.8
	H_2	6.1	5.7	4.6	4.1
	CH_4	7.0	6.6	6.4	6.4
	C_2H_6	0.7	1.1	1.2	1.6
	C_3H_8	4.2	5.6	9.0	13.1
	C_2H_4	6.0	6.2	5.4	5.6
	C_3H_6	1.2	1.5	1.7	1.8
	CO	3.7	2.1	2.4	2.9
	CO_2	7.5	7.2	6.5	5.4
Percent Expansion of Hydrocarbon Feed %		107.1	69.1	45.8	32.4

TABLE 4 (cont.'d)

Surface Combustion Propane Pyrolysis Data

Percent Propane Reacted	%	66.6	63.5	52.0	42.9
Oxygen Balance	%	11.3	+2.5	+1.3	-4.2
Hydrogen Balance	%	+0.9	-5.1	-8.0	-7.0

Yields Moles/(100 moles Hydrocarbon
           Feed)

C_2H_4	47.2	40.2	28.9	24.1
C_3H_6	9.5	9.4	8.9	7.7
CH_4	55.2	43.0	33.8	27.2

Carbon Distribution in Product %

C_2H_4	45.8	41.6	35.7	36.3
C_3H_6	13.7	14.6	16.5	17.5
CH_4	26.7	22.2	21.0	20.6
CO	12.6	4.2	4.5	3.1
C_4+ (including Carbon)	1.1	17.4	22.3	22.6

TABLE 5

Surface Combustion Propane Pyrolysis Data

Series R - 13

Run No.		3	4	5
Fuel Gas Rate	(lb. moles)/hr.	0.17	0.18	0.18
Air Rate	(lb. moles)/hr.	1.69	1.69	1.69
Molal Ratio	(Fuel and Air)/feed	5.02	4.01	3.21
Gas Temperatures $^\circ$F				
Top of Reaction Zone		1569	1355	1196
Middle of Reaction Zone		1701	1567	1441
Bottom of Reaction Zone		1600	1476	1383
Average of Reaction Zone		1623	1466	1340
Exit of Reaction Zone		1402	1303	1233
Off Gas Composition				
N_2		62.0	60.1	59.4
O_2		1.7	1.2	1.4
H_2		7.0	5.3	5.2
CH_4		6.9	6.1	4.8
C_2H_6		0.7	1.0	1.2
C_3H_8		4.7	9.5	13.7
C_2H_4		6.1	5.3	4.6
C_3H_6		1.0	1.7	1.2
CO		3.6	3.6	3.8
CO_2		6.2	6.2	5.6
Percent Expansion of Hydrocarbon Feed %		88.9	55.3	30.7
Percent Propane Reacted %		68.9	48.8	41.0

TABLE 5 (cont.'d.)

Surface Combustion Propane Pyrolysis Data

Oxygen Balance %	+5.0	+5.2	∓ 0
Hydrogen Balance %	-10 .4	-5.3	-10.0
Yields Moles/(100 moles Hydrocarbon Feed)			
C_2H_4	40.6	28.6	20.2
C_3H_6	6.9	9.0	5.1
CH_4	46.0	33.1	20.7
Carbon Distribution In Product %			
C_2H_4	37.4	37.1	32.2
C_3H_6	9.3	17.5	12.1
CH_4	21.2	21.4	16.5
CO	7.2	7.3	4.0
C_4+ (Including Carbon)	24.9	16.7	35.2

the furnace was not operable at ratios higher than 5 to 1.

The main variables investigated were space velocity (or residence time) and fuel-to-feed ratio. Although temperature was not an independent variable, it was measured.

To obtain an idea of the flow conditions, the range of Reynolds numbers existing in the reactor for the series of tests was calculated. The lowest Reynolds numbers existed at the entrance to the heated section where propane alone was present; the highest Reynolds numbers were at the exit where both the reaction and combustion gases were flowing. For all the runs, the Reynolds number ranged from 150 to 1500. This would indicate that mixing due to flow turbulence alone would be small. However, since end effects are undoubtedly large and since the combustion gases and the reactant gases flow into each other at right angles, it is believed that mixing is fairly complete.

Space velocities are not meaningful as a measure of reaction time in a reactor of the type used here since combustion gases enter the reaction zone all along the reactor length. However, they do give an indication of reactor capacity. Based upon gas volumes measured under standard conditions, and on the basis of the hydrocarbon feed alone, the space velocities ranged from 0.05 to 0.23 reciprocal seconds. On the basis of total feed (including both hydrocarbon feed and combustion gases), the space velocities ranged from 0.43 to 1.0 reciprocal seconds.

The reliability of the data is indicated by examination of the material balances. First of all, a nitrogen balance was written and the off-gas rates adjusted to this balance. In general, the nitrogen balances checked to within 5 percent. The other elemental balances were then calculated. Carbon balances do not give the true picture because only the

gaseous products (up to 3 carbon atoms) were metered and analyzed, while the higher hydrocarbons and free carbon were not collected. Oxygen balances were written assuming that the water formed during combustion remained in the off-gases. The oxygen balances generally agreed to within 5 percent and showed no trends. Losses of hydrogen ranging from 4 to 10 percent and averaging about 7 percent were shown by the hydrogen balances. These losses may be attributed to the hydrogen in the higher hydrocarbons and liquids that were not accounted for.

In autothermic cracking the overall product yields are controlled primarily by energy considerations. The heat produced by combustion of the fuel shows up in two places - as sensible heat in the off gases and as the heat of reaction in converting part of the hydrocarbon feed. Since pyrolysis occurs over a relatively narrow temperature range, the magnitude of variation in sensible heat content is small compared to the heat of reaction. The heat available for reaction per unit of feed depends on the fuel-to-feed ratio, and therefore, this ratio is the principal variable in determining the fractional conversion of the hydrocarbon feed. The temperature in the reactor automatically adjusts itself to a level such that the kinetic considerations are satisfied. Severity of cracking may be measured by the percent expansion of the original hydrocarbon feed.

Figure 15 shows the dependence of percent expansion on fuel-to-feed ratio rather than on space velocity. In this figure percent expansion of the propane feed is plotted against the fuel-to-feed ratio for the runs that had a three-fold variation in space velocity. The data fell on one curve - the minor deviations can be explained on the basis of heat losses and differences in the preheating.

Individual product yields of methane, ethylene, and propylene are plotted in Figure 16. Following the general practice in the literature, the fractional conversion of the propane feed was used as the correlating variable rather than temperature or space velocity. In a short reactor of this type, where large temperature gradients exist both along and normal to the direction of flow, temperature would not be expected to give a satisfactory correlation. Also in a reactor where the bulk of the gas stream enters along the whole length of the reactor, space velocity has very little real significance. Fractional conversion is a measure of the severity of cracking. As may be expected there is some scattering of data; but, on the whole the curves indicate the expected trends. With increasing severity of cracking, methane and ethylene yields increase while propylene yields decrease markedly. The high fractional conversions occur at high fuel-to-feed ratios and in these cases, the temperatures in the reactor are also relatively high. High temperatures, of course, favor the production of ethylene over propylene.

The product yields obtained in this investigation are compared to those from other industrial processes (tubular reactor, the lead bath reactor, and the conventional autothermic reactor) in

FIG. 15

EXPANSION OF HYDROCARBON FEED
VS. MOLAL RATIO

EXPANSION %

MOLAL RATIO $\left(\dfrac{AIR + GAS}{PROPANE}\right)$

▽ Series R - 11
□ Series R - 12
○ Series R - 13
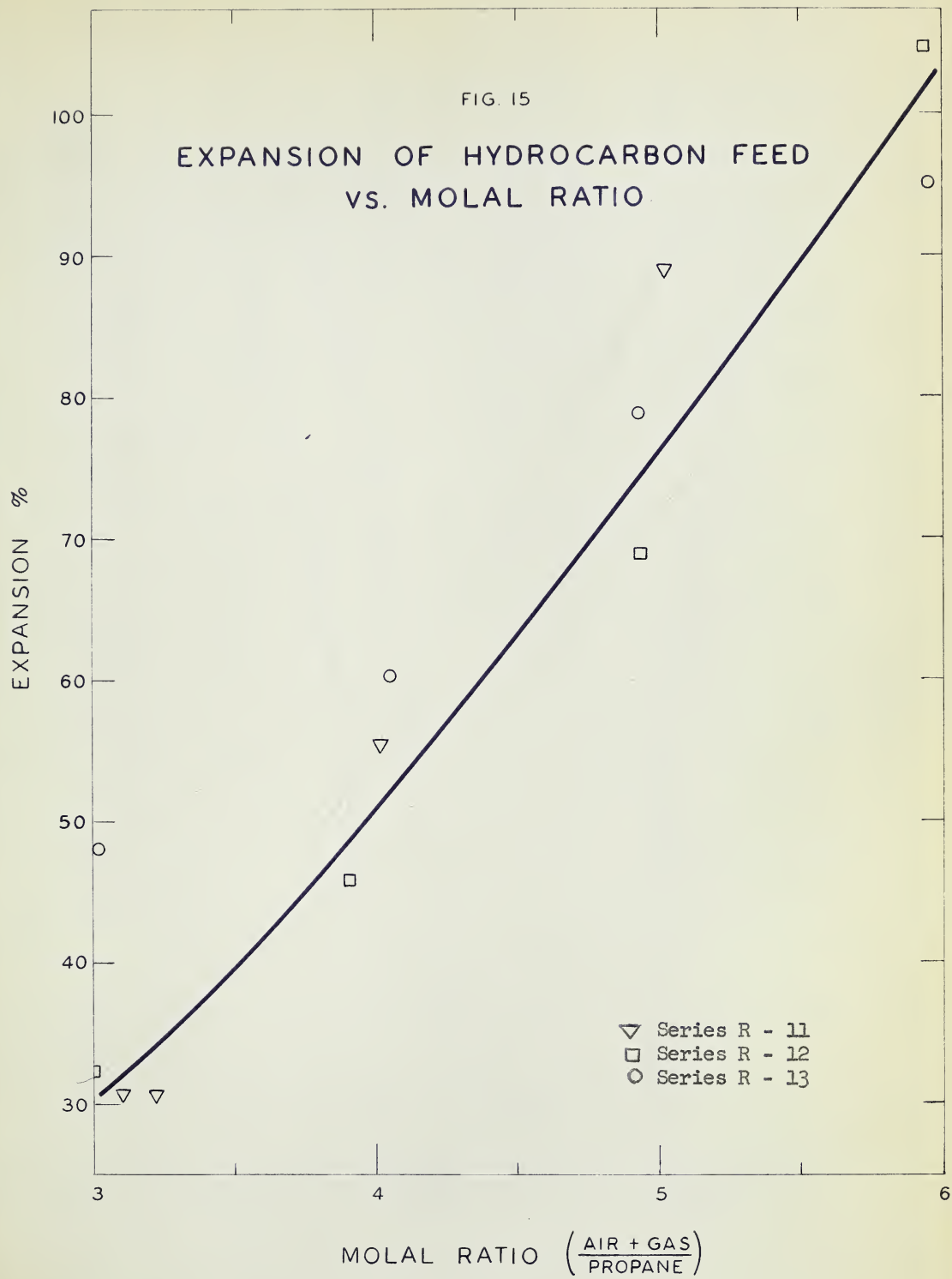
FIG. 16

PRODUCT YIELDS OF METHANE, ETHYLENE, AND PROPYLENE
IN SURFACE COMBUSTION REACTOR
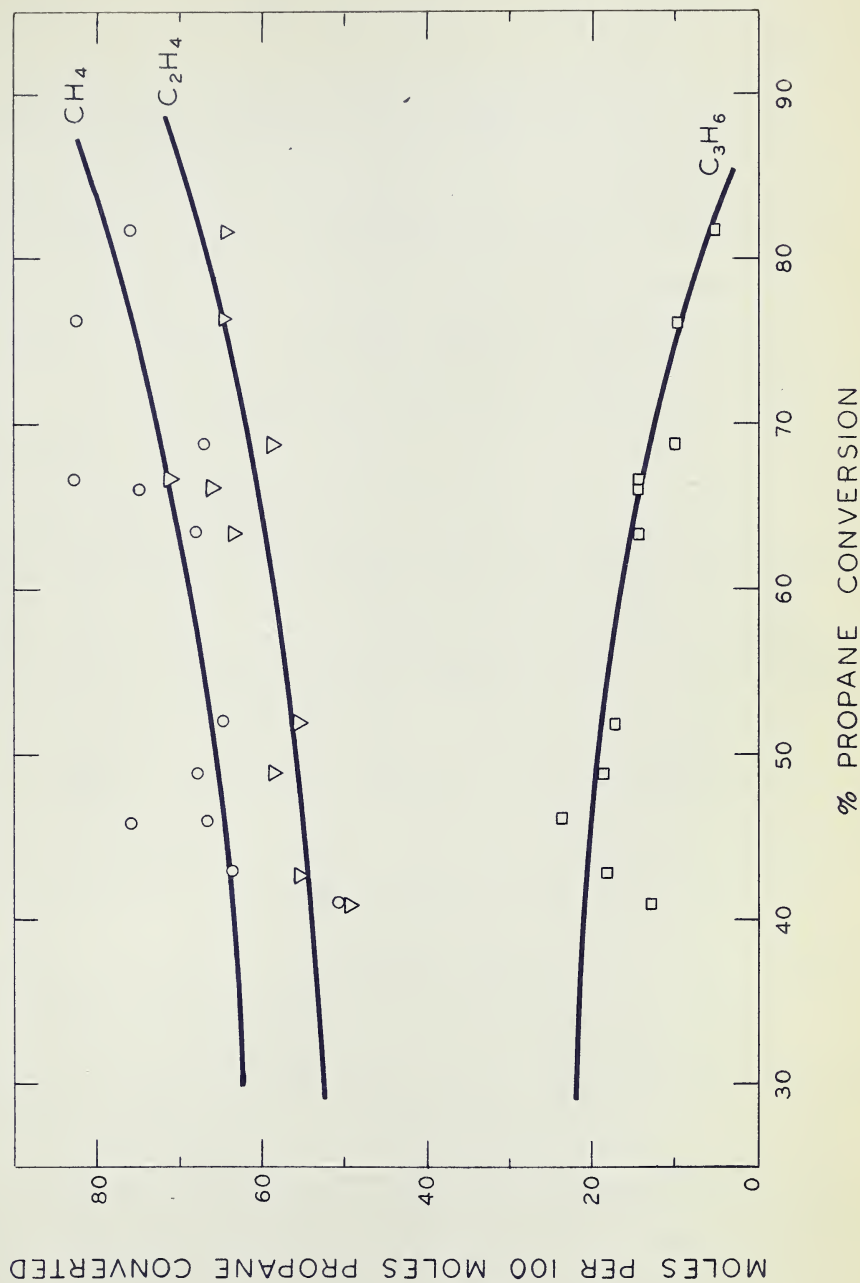
Figures 17, 18 and 19. It should be noted that the yields are
expressed in terms of the propane feed, and not the propane react-
ed as in Figure 18. The methane and ethylene yield curves are in
the same range as the other industrial processes. Within the limits
of experimental error, it may be concluded that the yields from all
those different processes are roughly the same. The propylene yields
as shown in Figure 19 for this reactor are considerably lower than
for the other processes with the maximum occurring at approximately
the same percent conversion. The lower propylene yields may be
attributed to the higher temperatures used in this reactor as compar-
ed to the others.

These higher temperatures are also probably responsible
for the high conversion of the carbon in the feed to the higher mole-
cular weight hydrocarbons (C_4+) as well as to carbon black (which may
be regarded as a high molecular weight hydrocarbon with a low hydrogen
content). At the high conversions the literature shows a C_4+ yield
of up to 15 percent of the carbon converted. In this investigation
the yield was as high as 25 percent. The rate of hydrocarbon decomposition
ranges from 1.6 to 5.5 lb. moles of propane cracked per cubic foot of
reactor space. This range of hydrocarbon decomposition rates is higher
than that for the tubular reactor (1.2 to 1.8 lb. moles of propane
cracked per cubic foot of reactor space) due to the better heat transfer
characteristics of the surface combustion autothermic type of reactor.

Thermal analysis of the data are presented in Tables 6, 7 and 8.
The heat losses in the experimental furnace are of two types - heat losses
to surroundings and heat losses due to the reforming reactions(the theoret-
ical heat available was calculated on the assumption of complete combustion).
Table 9 gives a breakdown of the heat losses into these two categories.
The bulk of the heat losses are to the surroundings. However, in a "scaled-
up" industrial

FIG.17

METHANE PRODUCTION vs. % CONVERSION

AUTOTHERMIC REACTOR

SURFACE COMBUSTION REACTOR

LEAD BATH REACTOR

TUBE REACTOR

MOLES PER 100 MOLES PROPANE CHARGED
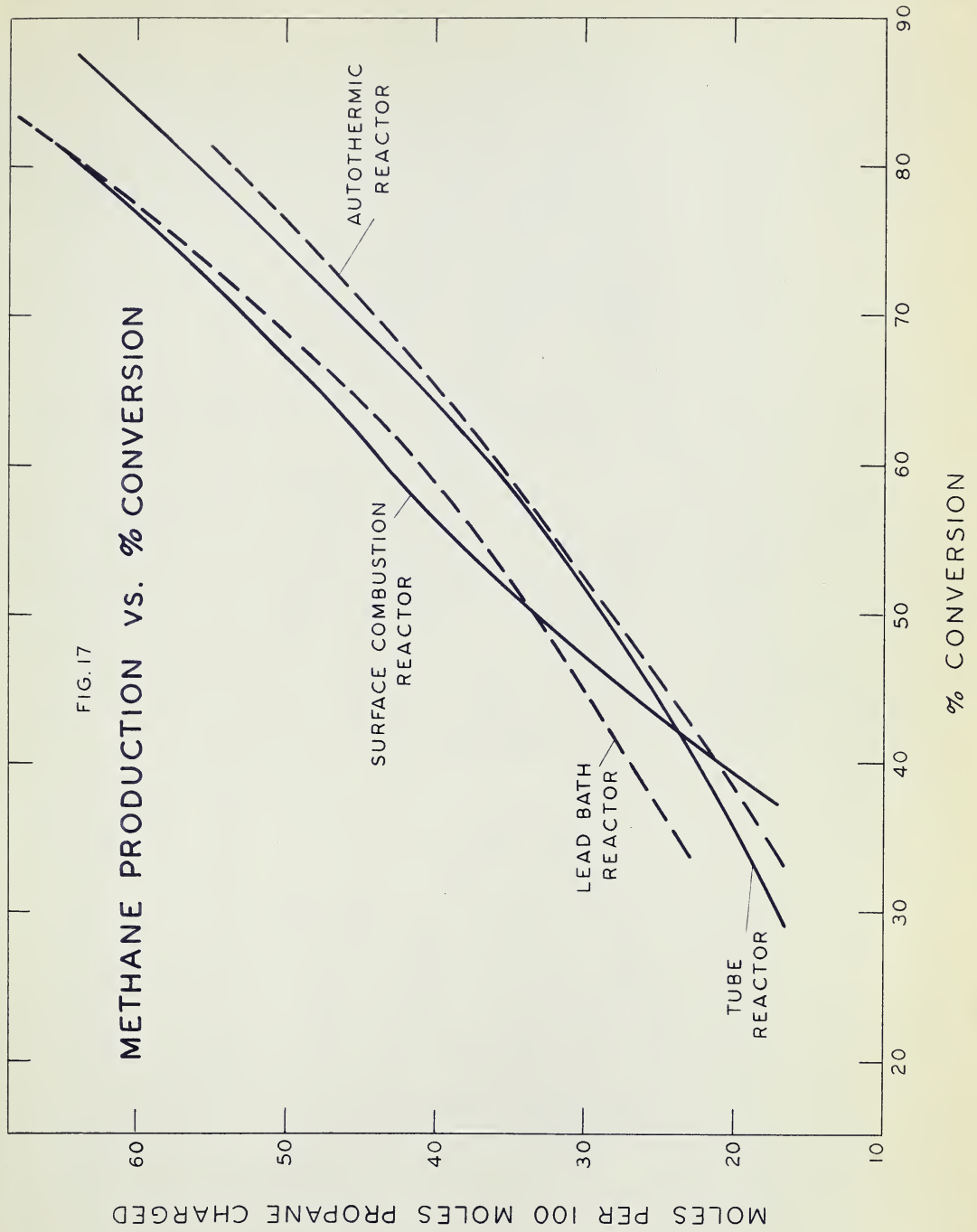
% CONVERSION

FIG. 19

PROPYLENE PRODUCTION
VS. % CONVERSION

LEAD BATH
REACTOR

AUTOTHERMIC
REACTOR

TUBE
REACTOR

SURFACE COMBUSTION
REACTOR

MOLES PER 100 MOLES PROPANE CHARGED

% CONVERSION

FIG. 18

ETHYLENE PRODUCTION VS. % CONVERSION
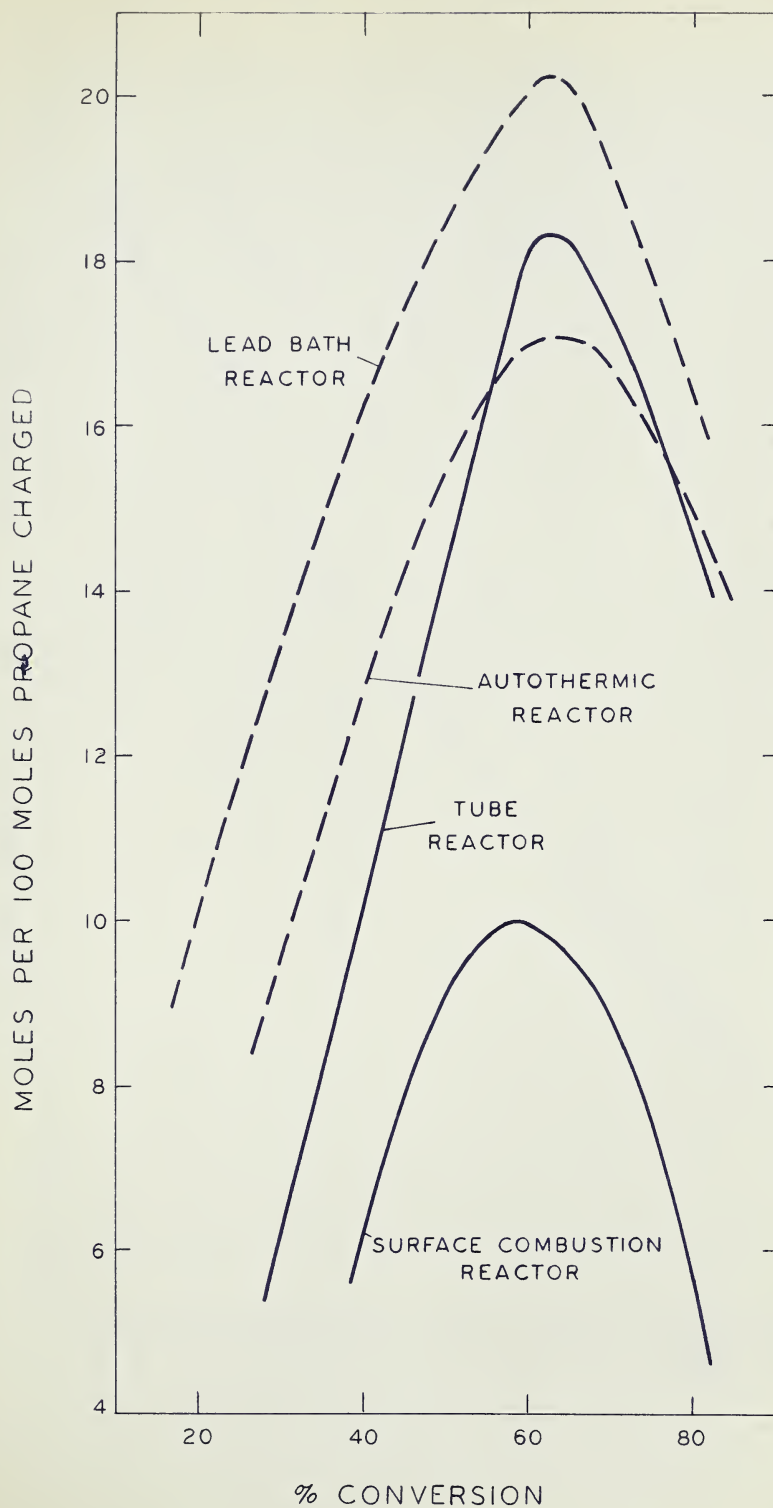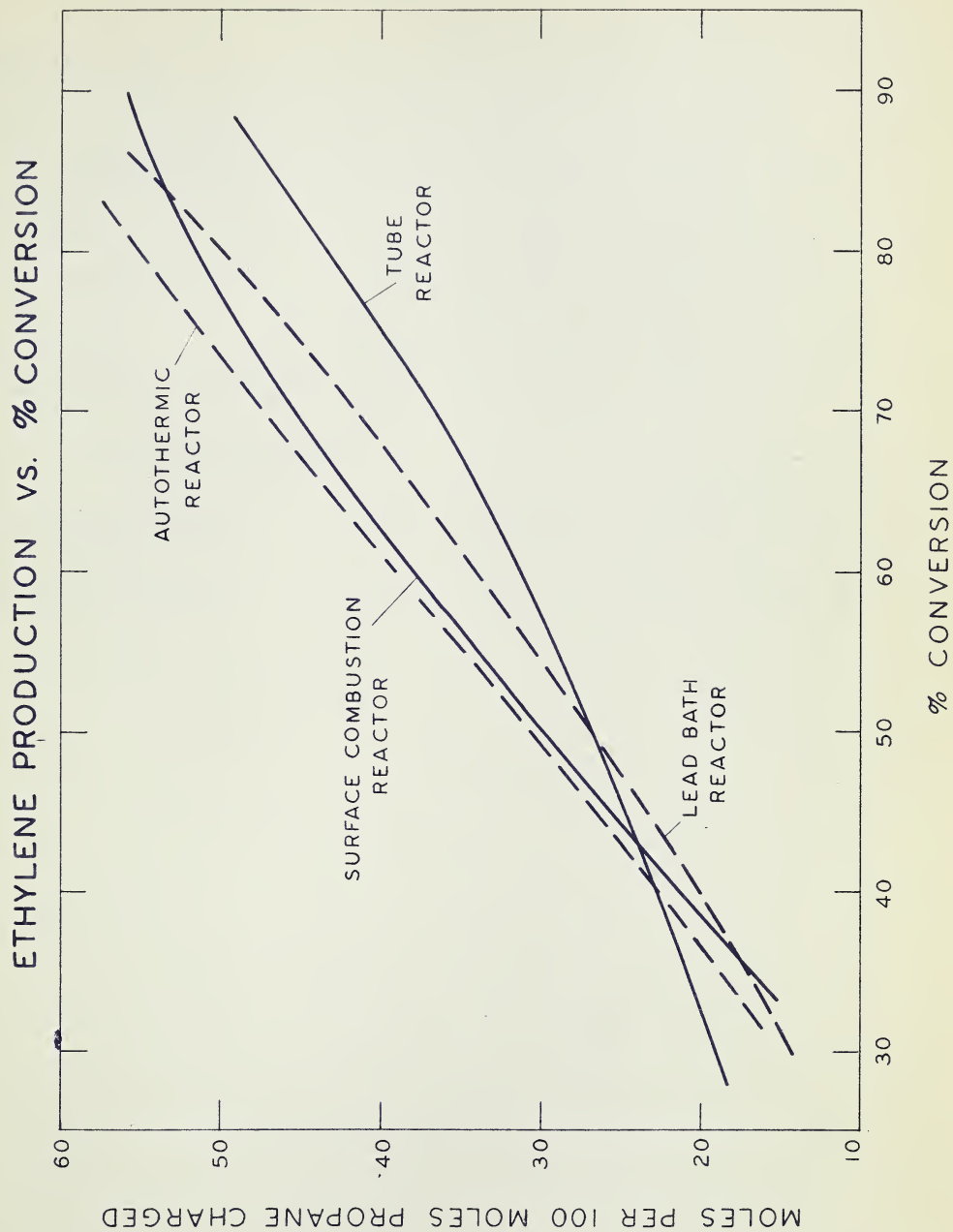
TABLE 6

Thermal Analysis

Series R - 11

Run No.	2	3	4	5
Fuel Gas Rate moles/hr	0.070	0.070	0.070	0.070
Air Rate " "	0.67	0.670	0.67	0.67
Air and Fuel " "	0.74	0.74	0.74	0.74
Molal Ratio	5.95	4.93	4.04	3.04
Total Flow Rate, moles/hr	0.865	0.89	0.92	0.98
Heat Lost M BTU/lb.mole to to ml. feed	10.34	9.31	7.18	3.99
Heat Lost M BTU/hr.	8.95	8.40	6.60	3.91
Thermal Efficiency %	48.2	51.8	61.5	74.1

TABLE 7

Thermal Analysis

Series R - 12

Run No.	5	2	3	4
Fuel Gas Rate moles/hr	0.12	0.12	0.12	0.12
Air Rate " "	1.18	1.18	1.18	1.18
Air and Fuel " "	1.30	1.30	1.30	1.30
Molal Ratio	5.93	4.93	3.90	3.00
Total FlowRate " "	1.518	1.564	1.605	1.732
Heat Lost M BTU/lb.mole total feed	12.84	10.86	8.20	5.07
Heat Lost M BTU/hr.	19.50	17.01	13.18	8.79
Thermal Efficiency %	37.1	46.7	55.5	69.2

TABLE 8

Thermal Analysis

Series R - 13

Run No.	3	4	5
Fuel Gas Rate	0.17	0.18	0.18
Air Rate	1.69	1.69	1.68
Air and Fuel	1.86	1.87	1.86
Molal Ratio	5.02	4.01	3.21
Total Flow Rate	2.232	2.336	2.437
Heat Lost M BTU/lb.mole total feed	8.37	9.01	6.16
Heat Lost M BTU/hr.	18.69	21.01	15.01
Thermal Efficiency %	54.2	52.7	64.3

TABLE 9

TABLE OF HEAT LOSSES AND THERMAL EFFICIENCIES

Run No.	Molal Ratio	Heat Loss Due To Sensible Heat	Heat Loss Due To CO Formation	Net Efficiencies
		%	%	%
R-11-2	6.0	49.5	2.3	48.2
R-11-3	4.9	45.5	2.7	51.8
R-11-4	4.0	35.5	3.0	61.5
R-11-5	3.0	20.2	5.7	74.1
R-12-5	5/9	62.1	0.8	37.1
R-12-2	4.9	51.8	1.5	46.7
R-12-3	3.9	42.4	2.1	55.5
R-12-4	3.0	27.0	3.8	69.2
R-13-3	5.0	42.9	2.9	54.2
R-13-4	4.0	44.3	3.0	52.7
R-13-5	3.2	32.2	3.5	64.3

reactor this type of heat loss can be reduced to almost negligible proportions. The heat losses due to the reforming reactions are un-avoidable, but are fortunately low. In the conventional autothermic process the CO-to-CO_2 ratios ranged from 1.8 to 2.5, whereas the ratios in this investigation ranged from 0.3 to 0.8. The lower ratios mean that higher thermal efficiencies are intrinsically possible. The difference in the range of values is explained on the grounds that in the conventional autothermic process, the combustion is carried out with an excess of hydrocarbon, while in the process described here the combustion utilizes a stoichiometric mixture of fuel and air, and the endothermic reforming reactions occur later. The heat generated by the burner in this (Surface Combustion Autothermic Reactor) reactor was between 18 to 46 thousand BTU per hour square foot. Comparing this with the heat fluxes encountered in the tubular reactor (8 to 10 thousand BTU per hour square foot) the heat fluxes are 2 to 6 times greater. The higher heat flux in the surface combustion reactor accounts for its generally higher rate of ethylene production. From an industrial point of view, this means a more compact reactor. It is believed that other types of surface combustion burners will give even higher fluxes.

It is noted that the best thermal efficiencies were obtained with the lower fuel-to-feed ratios. The temperature inside the reactor for the latter were in general one to two hundred Fahrenheit degrees lower; consequently the heat losses were also lower.

The composition of the off-gases are not representative of what may be expected from a larger unit in view of the high heat losses in this experimental unit. Table 10 shows the reduction in fuel-to-feed

TABLE 10

Comparison of Actual and Theoretical Fuel-to-Feed Ratios

Run No.	Conversion of Feed %	Actual Thermal Efficiency %	Actual Fuel-to-Feed Ratio	Computed Fuel-to-Feed Ratio	
				Case 1*	Case 2 **
R-11-2	81.8	48.2	6.0	3.0	1.9
R.-11-3	76.3	51.8	4.9	2.7	1.6
R-11-4	66.1	61.5	4.0	2.6	1.6
R-11-5	46.1	74.1	3.0	2.4	1.4
R-12-5	66.6	37.1	5.9	2.2	1.2
R-12-2	63.5	46.7	4.9	2.3	1.3
R-12-3	52.0	55.5	3.9	2.3	1.2
R-12-4	42.9	69.2	3.0	2.2	1.2
R-13-3	68.9	54.2	5.0	2.9	1.8
R-13-4	48.8	52.7	4.0	2.3	1.2
R-13-5	41.0	64.3	3.2	2.2	1.1

*Heat Losses To Surroundings Negligible; Feed Enters at 77° F

** Heat Losses To Surroundings Negligible; Feed Enters at 1000° F

ratio for various assumed operating conditions which would give the same overall conversion.

It is assumed that the fuel gases supply the heat necessary for the pyrolysis, but otherwise have no effect on the reaction. Theoretically much lower fuel-to-feed ratios are possible than were actually used in the present investigation, resulting in an off-gas several times richer in ethylene and propylene. There would be no difficulty in preheating the propane feed to 1000° F. Preheating the air and natural gas could result in even lower fuel-to-feed ratios, but this may lead to "flash-back" problems in the operation of the surface combustion burner. Hence this case was not analyzed theoretically.

CONCLUSIONS

No difficulty was encountered in the operation of the process. The presence of reacting hydrocarbon in the reaction zone did not have any noticeable effect on the operation of the burner. Thus the surface combustion burner gives complete combustion at relatively low temperatures in an atmosphere of hydrocarbons. However, as the molal ratio is decreased the reaction zone temperature also decreased.

Whenever the temperature in the reaction zone reached 1800 to 1900° F a "flash-back" occurred. This indicates that the upper temperature limit of the Cox surface combustor used was about 1900°F.

With the exception of propylene, the product distribution obtained from this investigation agreed within experimental error with those from the other processes. However, this discrepancy may be explained by the different temperature levels at which the various processes are carried out. Since the product distribution and yields from propane pyrolysis in the autothermic surface combustion process are approximately the same as those for other industrial processes, this seems to indicate that the manner in which the heat is supplied has no effect on the product distribution.

Due to the large heat losses, thermal efficiencies in the present experimental unit are low. However, most of the heat losses were of the type that could be reduced to negligible proportions in a large industrial unit. These heat losses that may be reduced comprise approximately 94% of the heat lost. The other 6% of the heat lost is used in the reforming reactions and cannot be reduced.

Because of the lower CO to CO_2 ratios the present process should have

higher thermal efficiencies than the conventional autothermic process.

No attempt has been made to evaluate the economics of the

process used. However, in view of the compactness of the reactor, the

simplicity of the reaction furnaces, and the potentially high thermal

efficiencies it is believed that the process investigated has indust-

rial possibilities.

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A P P E N D I X

A. EXPERIMENTAL PROCEDURE

        Before an experimental run is started there is some prelim-
inary work that must be done. This work is as follows:

        1. Calculations are made of the various gas flows

        These calculations are corrected to the conditions existing
on the day of the experimental run.

        2. The oxygen analyser is turned on at least 24 hours before
the run is started so that the detecting unit is at thermal equilibrium
when the analyser is used. On the day of the run a Varian Recorder that
has been standardized is connected to the analyser. This oxygen analys-
ing unit (Oxygen Analyser and Varian Recorder) is calibrated with two
gases, purified nitrogen and air (20.93% O_2).

        3. The temperature recorder and cooling water to the heat ex-
changer are turned on. The off-gas meter is by-passed.

        4. The furnace is lit by inserting the lighting torch through
the observation port hole. It must be noted that the torch is inserted
before the natural gas is turned on. The air ejector is adjusted so that
there is a slight negative pressure in the furnace during the lighting.
The fuel gas mixture on lighting the furnace is such that there is an
excess of natural gas in order to facilitate lighting. After the burner
is lit the fuel gas rates are adjusted to the desired values and the fur-
nace pressure is adjusted to atmospheric pressure.

        Thus the furnace is operating without any propane (reactor gas)
passing through the unit. If desired, it is possible to take a sample of
this gas in order to check the analysis with a carbon balance, etc.
Using this run, it is possible to calculate the percent expansion of

the reacting hydrocarbon in the following runs. The sample must be
taken as quickly as possible and then the reacting hydrocarbon is let
into the system. This is necessary because the furnace heats up very
quickly when there is no reacting hydrocarbon passing through the system.

After the propane (reacting hydrocarbon) is let into the
system it is only necessary to adjust the pressure and maintain it in
the furnace at atmospheric pressure. During a series of runs the fuel
gas rate will be kept constant, thus only the reacting hydrocarbon flow
rate and the furnace pressure need adjusting for individual runs.

Once all of the flow rates (including the off gas) and the
recorded temperatures are constant (criterion of steady state) a sample
may be taken. All of the pertinent information is recorded and the time
of sampling noted.

Theoretical Temperature Distribution Within A Burner Plate

Assume that the gaseous mixture of air and fuel gas is at
thermal equilibrium with the burner plate at all times (steady state)
and the product GC_p is independent of distance.

An energy balance on a unit cross-section dx thick and a
distance x from the combustion zone is

$$OC_p (T-Ta) - GC_p(T-dT-Ta) = k \frac{dT}{dx} - k(\frac{dT}{dx} + \frac{d^2 T}{d x^2} dx) + r(\Delta H)....(1)$$

Assuming no reaction takes place in the preheat zone the equation
reduces to

$$GC_p \ dT = -k \frac{d^2 T}{dx^2} \ dx \ ....(2)$$

and

$$\frac{GC_p}{k} \frac{dT}{dx} + \frac{d^2 T}{dx^2} = 0 \ ....(3)$$

Let $\frac{GC_p}{k} = \alpha$, and y $= \frac{dT}{dx}$

then $\frac{dy}{dx} = \frac{d^2T}{d\,x^2}$

By substituting the above into equation (3) you get

$$\alpha y + \frac{dy}{dx} = 0 \dots\dots\dots\dots\dots\dots\dots(4)$$

Integrating equation (4)

$$ye^{\alpha x} = c_1 \dots\dots\dots\dots\dots\dots\dots(5)$$

Substituting for y

$$\frac{dT}{dx}\,e^{\alpha x} = C_1 \dots\dots\dots\dots\dots\dots\dots(6)$$

$$dT = C_1 e^{-\alpha x}dx \dots\dots\dots\dots\dots\dots\dots(7)$$

Integrating equation (7)

$$\int_T^{Ts} dT = C_1 \int_{x=x}^{x=o} e^{-\alpha x}\,dx \dots\dots\dots\dots\dots\dots(8)$$

Thus $(Ts - T) = = \frac{-C_1}{\alpha}(1 - e^{-\alpha x}) \dots\dots\dots\dots\dots\dots(9)$

But at $x = \infty$, $T = Ta$

and $(Ts - Ta) = -\frac{C_1}{\alpha}(1 - 0) \dots\dots\dots\dots\dots\dots(10)$

Therefore, $(Ts - Ta) = -\frac{C_1}{\alpha} \dots\dots\dots\dots\dots\dots(11)$

Substituting equation (11) into equation (9) for $-\frac{C_1}{\alpha}$,

you get $(Ts - T) = (Ts - Ta)(1 - e^{-\alpha x})$

Rearranging

$$\frac{Ts - T}{Ts - Ta} = 1 - e^{-\alpha x}$$

Table 11 is constructed for various values of T at various values

of x using the following assumption:

Ts = 2000° F

Ta = 100° F

k = 1/6 BTU/(hr)(ft)($^{\circ}$F)

C_p = 0.275 BTU/(lb)($^{\circ}$F)

NOMENCLATURE

C_p = heat capacity of gaseous mixture, BTU/(lb)($^{\circ}$F)

k = thermal conductivity of burner material BTU/(hr)(ft)($^{\circ}$F)

G = mass rate of flow of gaseous mixture Lb/(hr)(ft^2)

Ta = temperatures of entering air and fuel (in this case room temperature) $^{\circ}$F

Ts = Surface temperature in combustion $^{\circ}$F

X = distance behind combustion surface of burner plate Ft

r = rate of conversion of hydrocarbon feed lb/(hr)(ft.^{3}reactor volume)

ΔH = heat of reaction BTU/(lb. converted)

TABLE 11

### Calculation Table for Temperature Distribution Through A Burner Plate

G	12X ins.	C_p	k	$= \dfrac{GC_p}{k}$	x	e^{-x}	$1-e^{-x}$	$T_B(1-e)^*$	T^{**}
20	0.1	0.275	2/12	33.850	0.282	0.754	0.246	467	1533
	0.2				0.564	0.569	0.431	819	1181
	0.4				1.128	0.324	0.676	1284	716
	0.6				1.693	0.184	0.816	1550	450
	0.8				2.257	0.105	0.895	1700	300
36	0.1			59.232	0.494	0.610	0.390	741	1259
	0.2				0.987	0.373	0.627	1191	809
	0.4				1.974	0.139	0.861	1636	364
	0.6				2.962	0.052	0.948	1801	199
	0.8				3.949	0.019	0.981	1864	136
50	0.1			84.615	0.705	0.494	0.506	961	1139
	0.2				1.410	0.244	0.756	1436	564
	0.4				2.820	0.060	0.940	1786	214
	0.6				4.231	0.014	0.986	1873	127
	0.8				5.641	0.004	0.996	1892	108
180	0.05			296.158	1.234	0.291	0.709	1347	653
	0.10				2.648	0.085	0.915	1738	262
	0.20				4.936	0.007	0.993	1887	113

* $T_B = T_s - T_a$

** $T = 2000 - (T_s - T_a)(1 - e^{-x})$

C   Heat Loss Through Walls of Furnace
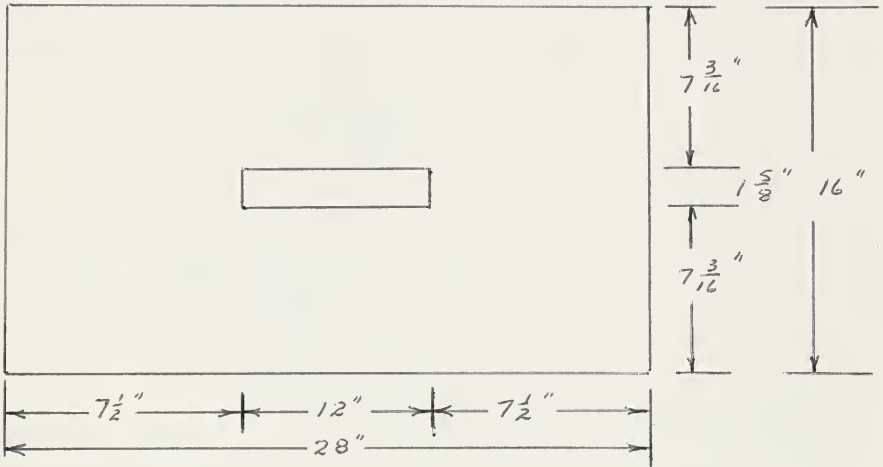
Basis of Calculation:

1 foot of reactor height

$$Q = k A \frac{\Delta T}{X}$$

now $k = 0.3$ BTU/(hr. ft. $^\circ$F)

For the ends:

$$Q \text{ Area} = 1/12 \left[\frac{16 - 1.625}{\ln \frac{16}{1.625}} \right]$$

$$= 0.522 \text{ ft.}^2$$

Therefore, $Q = \frac{2(0.522)\ 0.3}{\frac{7.5}{12}} \Delta T$

$$= 0.501 \ \Delta T \quad \text{BTU/hr. ft.}$$

The factor 2 was put in beaause there are two ends.

For the sides:

$$\text{Area} = A = 1/12 \left[\frac{28 - 12}{\ln \frac{28}{12}} \right]$$

$$= 1.66 \text{ ft.}^2$$

$$Q = \frac{2(1.66)(0.3)}{\frac{7.19}{12}} \Delta T$$

$$= 1.525 \ \Delta T \quad \text{BTU/hr.}$$

Therefore the Total $Q = 1.525\ \Delta T + 0.501\ \Delta T = 2.026\ \Delta T$ BTU/hr.

Assuming that the temperature of the shell of the furnace is 180° F and that the average temperature of the bricks inside the furnace is $1323\ ^{\circ}$F then

$$Q = 2.026\ (1323 - 180) = 2316 \text{ BTU/hr.}$$

For a furnace height of 2 feet the heat loss through the walls of the furnace is

$$2(2316) = 4632 \text{ BTU/hr} = 4.63 \text{ M BTU/hr}$$

D   Computed Fuel-to-Feed (Molal) Ratio

Ha = heat available

L = heat loss to surroundings

N = Fuel-to-feed (molal) ratio

NF = total moles of air plus natural gas

$Ha-L$ = heat available for cracking

$\dfrac{Ha-L}{F}$ = heat available for cracking per mole of feed

$\dfrac{Ha}{NF}$ = heat available per mole of fuel gas (air plus natural gas)

Case 1. Neglecting heat losses

$$N' \quad = \quad \dfrac{\dfrac{Ha - L}{F}}{\dfrac{Ha}{NF}} \quad = \quad \dfrac{(Ha - L)}{Ha}\ N$$

Case 2. Neglecting heat losses and preheating the feed to 1000° F

(Preheating the feed to 1000° F requires 26000 BTU/lb. mole

$$N' \quad = \quad \dfrac{\dfrac{(Ha - L - 26F)}{F}}{\dfrac{Ha}{NF}} \quad = \quad \dfrac{(Ha - L - 26F)}{Ha}\ N$$

26 is used because Ha and L are in M BTU

TABLE 12

Comparison of Analytical Results

E

Component	R-11-4		R-2-2		R-13-3	
	G.C.*	M.S.**	G.C.*	M.S.**	G.C.*	M.S.**
H_2	5.5	5.8	5.7	0.3	7.0	5.2
N_2	59.4	61.1	62.9	68.1	62.0	69.3
O_2	1.0	0.1	1.0	0.3	1.7	0.4
CH_4	8.8	7.2	6.6	6.3	6.9	4.7
C_2H_6	1.3	1.0	1.1	0.7	0.7	0.4
C_3H_8	6.1	5.9	5.6	5.7	4.7	3.2
C_2H_4	7.6	9.2	6.2	8.6	6.1	6.4
C_3H_6	1.8	2.1	1.5	1.8	1.0	0.9
CO	2.4	2.4	2.1	2.1	3.6	3.6
CO_2	6.1	5.2	7.2	6.1	6.2	5.9

* G.C. = Gas Chromatography (Research Council of Alberta)

** M. S.= Mass Spectrometer (Canadian Chemical Company)
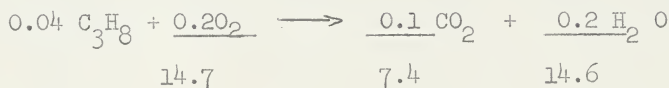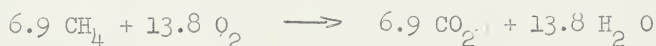
F. SAMPLE CALCULATIONS

Element Balances

Example R-11-4

Table 13 shows the method used to check the analysis against the flow rates. The air is assumed to be 21% Oxygen and 79% Nitrogen. All the other gases were analysed using gas chromatography.

Percent Expansion

Example R-11-4

Assumption: complete combustion of fuel gas

$$6.9 \ CH_4 + 13.8 \ O_2 \longrightarrow 6.9 \ CO_2 + 13.8 \ H_2O$$

$$0.2 \ C_2H_4 + 0.7 \ O_2 \longrightarrow 0.4 \ CO_2 + 0.6 \ H_2O$$

$$0.04 \ C_3H_8 + \underline{0.2O_2} \longrightarrow \underline{0.1} \ CO_2 + \underline{0.2 \ H_2O}$$

$$14.7 \qquad\qquad 7.4 \qquad\qquad 14.6$$

Oxygen entering reaction = 15.3 lb. moles

Oxygen used up by reaction = 14.7 lb. moles

Oxygen present in off gas = 0.6 lb. moles

TABLE 13

Material Balances on Data

Run R-11-4

Basis: 100 lb. moles of feed

Air = 72.5 lb. moles Gas = 7.6 lb. moles Propane = 19.9 lb. moles Off Gas = 97 lb. Moles

N_2 = 57.3 lb. moles N_2 = 0.3 lb. moles N_2 = 0.2 lb. moles

O_2 = 15.2 lb. moles O_2 = 0.1 lb. moles

                          CH_4 = 6.9 lb. moles

                          C_2H_6 = 0.2 lb. moles C_2H_6 = 2.3 lb. moles

                          C_3H_8 = 0.04 lb. moles C_3H_8 = 17.4 lb. moles

N_2 in = 57.8 lb. moles

N_2 out = 57.6 lb. moles

Error = -0.2 lb. moles

% Error = -0.35%

	In	Out (N$_2$ Bal. Corrected)	Carbon Balance (Atoms) In	Carbon Balance (Atoms) Out	Oxygen Balance (Atoms) In	Oxygen Balance (Atoms) Out	Hydrogen Balance (Atoms) In	Hydrogen Balance (Atoms) Out
H_2		5.4						10.8
N_2	57.8	57.8						
O_2	15.3	1.0			30.6	2.0		
CH_4	6.9	8.6	6.9	8.6			27.6	34.0
CO		2.3		2.3		2.3		
C_2H_6	2.5	1.3	5.0	2.6			15.0	7.8
CO_2		5.9		5.9		11.8		
C_2H_4		7.4		14.8				29.6
C_3H_8	17.4	5.9	52.2	17.7			139.2	47.2
C_3H_6		1.7		5.1				10.2
H_2O						14.6		29.2
Total			64.1	57.0	30.6	30.7	181.8	168.8
Error				-7.1		+0.1		-13.0
%Error				-11.1%		+0.32%		-7.2%

Nitrogen flowing	= 57.8 lb. moles
Carbon dioxide formed	= 7.4 lb. moles
Oxygen left over	= 0.6 lb. moles
Off gas due to combustion	= 65.8 lb. moles
Propane added	= 19.7 lb. moles
Total	= 85.5 lb. moles
Metered off gas	= 97.4 lb. moles
Total	= 85.5 lb. moles
Expansion	= 11.9 lb. moles

% Expansion $= \dfrac{11.9}{19.7} \times 100 \% = 60.4\%$

Percent Propane Reacted

Example	= R-11-4
Propane in feed	= 17.4 lb. moles
Propane in off gas	= 5.9 lb. moles
Propane reacted	= 11.5 lb. moles

% propane reacted $= \dfrac{11.5}{17.4} \times 100\% = 66.1\%$

Yields

Example: ethylene in R-11-4

Ethylene produced	= 7.4 lb. moles
Propane feed	= 17.4 lb. moles
Propane reacted	= 11.5 lb. moles

Ethylene yield $= \dfrac{7.4}{17.4} \times \dfrac{100}{100} = 42.5$ moles/(100 moles hydro-carbon feed)

$= \dfrac{7.4}{11.5} \times \dfrac{100}{100} = 64.4$ moles/(100 moles hydrocarbon reacted)

Carbon Distribution in Product

Basis: ethylene, propylene, methane, carbon monoxide, and carbon in product

Example = R-11-4

Constituent	Mole Percent	Atoms of Carbon	Percent Carbon
C_2H_4	7.4	14.8	40.1
C_3H_6	1.7	5.1	13.8
CH_4	8.6	8.6	23.3
CO	1.3	1.3	3.5
C	7.1	7.1	19.3
		36.9	100.0

Check:

Constituent	Moles Reacted	Carbon Atoms
C_2H_6	1.2	2.4
C_3H_8	11.5	34.5
		36.9

Thermal Efficiency

Basis: calculated combustion of air and fuel gas. Also 100 lb. moles

total flow (air and propane and fuel gas)

Example = R-11-4

Table 14 shows the calculations in detail, but these calculations do not

include the heat utilized to form CO from CO_2.

$$\text{Heat used } (CO_2 \text{ to } CO) = + 40 \text{ M BTU/lb. mole}$$

The CO_2 converted to CO is equal to the difference in the calculated

combustion reaction and the moles of CO_2 in the exit gas.

$$\text{Thus } CO_2 \longrightarrow CO = 7.4 - 5.9 = 1.5 \text{ lb. moles}$$

TABLE 14

Sample Thermal Efficiency Calculations

Basis of Calculation: 100 lb. moles of feed (Air, Natural Gas and Propane)

Air at 74.3° F

	Lb. Moles	M BTU/lb. mole	+	M BTU −
N_2	57.3	-0.01		0.6
O_2	15.2	-0.01		0.1
				0.7

Natural Gas at $75.1\ ^{\circ}$F

N_2	0.3	-0.01		
O_2	0.1	-0.01		
CH_4	6.9	-32.3		222.9
C_2H_6	0.2	-36.3		7.3
C_3H_8	0.04	-44.5		1.8
				232.0

Propane at 69°F

N_2	0.2	-0.03		
C_2H_6	2.3	-36.4		83.7
C_3H_8	17.4	-44.6		776.0
				859.7

Off Gas at 1323 $^{\circ}$F

H_2	5.4	8.6	46.4	
N_2	57.8	9.1	526.0	
O_2	1.0	9.1		
CH_4	8.6	-16.2		139.3
CO	2.3	-38.6		88.8
C_2H_6	1.3	-9.5		12.4
CO_2	5.9	-155.3		916.3

TABLE 14 (cont'd.)

C_2H_4	7.4	44.1	326.3	
C_3H_8	5.9	- 5.5		32.4
C_3H_6	1.7	+41.4	70.4	
H_2O	14.6	-112.0		1635.2
C	7.1	+4.97	35.3	
			1013.5	2824.5
				1810.9

Off Gas - Propane

N_2	57.6	9.1	524.2	
O_2	0.6	9.1	5.5	
CO_2	7.4	-155.3		1149.2
H_2O	14.6	-112.0		1635.2
			529.7	2784.4
				2254.7

H(Air and Gas) = -0.7 + (-232.0) = -232.7 M BTU

H (in) = -232.0 + (-0.7) + (-859.7) = -1092.4 M BTU

Heat Lost = -1810.9 + 1092.4 = -718.5 M BTU

Heat Available = -2254.7 + 232.7 = -2022.0 M BTU

% Heat Lost = $\dfrac{-718.5}{-2022.0}$ x 100 = 35.5%

Therefore, % Heat Eff. = 100 - % Heat Lost = 100 - 35.5 = 64.5%

Heat used $(CO_2 + CO) = (1.5)(+40) = +60$ M BTU

The available heat is reduced by 60 M BTU

And heat available $= -2022.0 + 60 = -1962.0$ M BTU

The heat loss $= \dfrac{718.5}{1962.0} \times 100\% = 36.6\%$

Thermal efficiency $= 100 - 36.6 = 63.4\%$

This correction is necessary because the CO is not formed during the combustion reaction.

Heat Loss

Example $=$ R-11-4

Basis: 100 lb. moles of total feed

From Table 14 heat loss $= 718.5$ M BTU

and heat loss $= 7.8$ M BTU/(lb. mole total feed

From Table 6 total feed flow rate $= 0.92$ lb. moles/hr

Therefore, heat loss $= 7.18$ $(0.92) = 6.60$ M BTU/hr

Heat loss due to CO formation

Example $=$ R-11-4

Heat Loss $(CO_2$ to CO$) = 60$ M BTU

$\%$ heat loss $= \dfrac{60}{2022.0} \times 100\% = 2.96\% = 3.0\%$

Computed Fuel-to-Feed Ratios

Example $=$ R-11-4

Ha $= 2022.0$ M BTU

L $= 718.5$ M BTU

N $= 4.04$

F $= 19.9$ lb. moles

Case 1. Assuming heat loss to surroundings is negligible

$$N' = \frac{(Ha - L)}{Ha} \qquad N = \frac{(2022.0 - 718.5)}{2022.0} \qquad 4.04 = 2.6$$

Case 2. Assuming heat loss to surroundings is negligible and feed preheated to 1000° F

$$N'' = \frac{(Ha - L - 26F)}{Ha} \ N$$

$$N'' = \frac{(2022.0 - 718.5 - 517.5)}{2022.0} \qquad 4.04 = 3.6$$

Calculation of Reynolds Number

$$Re = \frac{4\,R_H\,G}{\mu}$$

where Re = Reynolds number

     R_H = hydraulic radius ft.

     G = mass rate of flow lb mass/ft^2 sec.

     μ = viscosity lb mass/ft sec.

Using the propane feed of run R-11-2

     viscosity = 0.0261 centipoise

           = 1.755×10^{-5} lb mass/ft. sec.

     density = 0.1203 lb. mass/cu.ft.

     propane flow = 0.745 scfm.

           = 0.745 (0.1203)(60)(0.135)

           = 0.0111 lb. mass/ft.^{2} sec.

0.135 ft.^{2} is the cross-sectional area of the reaction zone

perpendicular to the rate of flow

     hydraulic radius = $\dfrac{ab}{2(a + b)}$ = $\dfrac{(1)(0.135)}{2(1 + 0.135)}$

           = 0.0594 ft.

     Re = $\dfrac{4(0.0594)(0.0111)}{1.755 \times 10^{-5}}$ = 150

Calculation of Space Velocities

Using the propane feed of run R-11-2 as an example.

     Propane feed = 0.745 scfm.

     Volume of reaction zone = 0.248 cu. ft.

Therefore, space velocity $= \dfrac{0.745}{0.248}$ min.$^{-1} = 3.00$ min.$^{-1}$

$= 0.05$ sec.$^{-1}$

Calculation of the Rate of Generation of Heat

Using run R-11-2 as an example:

The surface area of the burner is 1 sq. ft.

The following is used to calculate the time it takes for 100 lb. moles of total feed to flow.

Air flow = 4.02 scfm = 241.2 scfh

Gas flow = 0.417 scfm = 25.0 scfh

Propane flow = 0.745 scfm = 44.7 scfh

Total flow = 310.9 scfh

310.9 scfh/(359 cu.ft./lb.mole) = 0.865 lb. moles/hr.

It takes 100 lb. moles 100/0.865 or 115.3 hrs. to flow

Heat generated by the fuel gas = 2089.9 M BTU/(100 lb. moles)

Therefore heat generated = 2089.9/115.3 = 18.1 M BTU/hr.(sq.ft.)

Calculation of Rate of Hydrocarbon Decomposition

Characteristic of the reactor = 3.995 sq. ft. of reactor/cu.ft.

Using run R-11-2 as an example

Heat generated = 2089.9 M BTU/100 lb. mole

Heat lost = 1081.7 M BTU/100 lb. moles

Heat available for thermal decomposition = 1008.2 M BTU/100 lb. moles

= 1008.2/115.3 = 8.7 M BTU/hr. sq. ft.

Heat of cracking = 40 M BTU/lb. mole

Rate of hydrocarbon decomposition $= \dfrac{8.7}{40}$ X 3.995 = 1.6 lb. moles of propane/hr. (cu.ft.)